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**PHOTOCHEMICAL TRANSFORMATIONS OF SELECTED
OXYGEN AND NITROGEN HETEROCYCLES**

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

UGS001

by

D. RAMAIAH

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

FEBRUARY, 1988

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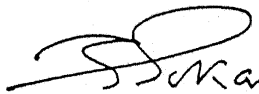
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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


D. Ramaiah

ACKNOWLEDGEMENTS

It is with great pleasure that I place on record my deep sense of gratitude to Professor M. V. George for suggesting the research problem and for encouraging me to a successful completion of this work. Also, I wish to express my thanks to Dr. P. K. Das of the Radiation Laboratory of the University of Notre Dame, for carrying out the laser flash photolysis and pulse radiolysis studies, reported in this thesis.

My sincere thanks are due to Professor P. S. Goel, Professor S. Chandrasekaran, Professor S. Ranganathan, Professor V. Chandrasekar and all other members of the Chemistry faculty, for their encouragement and interest in my progress.

My thanks are also due to all friends and colleagues in the Department of Chemistry and in particular, I would like to thank Drs. K. Ashok, S. Prathapan, M. Muneer and K. R. Gopidas for all the help they rendered to me.

I sincerely acknowledge with thanks the help rendered by Messrs N. Ahmad, K. Rajagopalan and the staff of the Chemistry Department Office, Chemistry Stores, Chemistry Workshop, Central Library, Central Glass Blowing Workshop and Graphic Arts Section. My sincere thanks are due to Mr. B. L. Shyamal for his ready and unreserved help throughout my stay here.

Thanks are due to Mr. C. M. Abraham for the typing of the thesis, Mr. B. K. Jain and Mr. R. K. Bajpai for the drawings and Mr. Mumtaz Ahmed for binding.

My thanks are due to the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore and the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow for recording several of the NMR and Mass Spectra reported in this thesis.

Financial assistance from the authorities of I.I.T. Kanpur in the form of a Research Fellowship is gratefully acknowledged.

Finally, I wish to express my indebtedness and gratitude to my parents, brothers and sisters for their constant support and encouragement.

Kanpur
February, 1988

D. Ramaiah

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PREFACE

The thesis entitled: "Photochemical Transformations of Selected Oxygen and Nitrogen Heterocycles" consists of three chapters.

Chapter I deals with our studies on the phototransformations of epoxyindanone adducts such as 6,7-dibenzoyl-8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19a), dimethyl 8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (19b), methyl 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6-carboxylate (19c), 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19d), 8,9-dihydro-5,6,7,8-tetraphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19e), and dimethyl 8,9-dihydro-5-methyl-8-phenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (22).

Irradiation of 19a-c in solvents such as acetone, benzene and a mixture (1:9) of benzene and methanol exhibited singlet state-mediated photoisomerization leading to 2,5-diphenylindeno[1,2-b]furan-4-ones 25a-c in good yields. However, irradiation of 19d and 19e in benzene and in a mixture (1:9) of benzene and methanol exhibited triplet state-mediated reactions leading to naphthalene derivatives 26d and 26e, respectively, in addition to the singlet state-mediated products 25d and 25e. Under the conditions of workup, both 26d and 26e were isolated

as 27d and 28e, respectively. In contrast, the irradiation of 19d in acetone gave mostly 27d. Interestingly, the formation of 27d was completely suppressed, when the irradiation of 19d was carried out in air-saturated benzene. Irradiation of 22 in acetone, benzene and methanol gave the naphthalene derivative 32, most probably via singlet state-mediated pathways. Thermal transformations of 19a and 19b, on the other hand, gave decarboxylated products such as 39a,b, in addition to the indenofurans 25a,b. Nanosecond, laser excitation of 19a-e gave transient absorptions, tentatively assigned to biradicals from Norrish type I photocleavage. In some cases, triplets acting as precursors for the di- π -methane rearrangement leading to naphthalene derivatives have been observed under energy-transfer excitation.

The results of our investigations on the phototransformations of benzoylaziridines are described in Chapter II. The substrates studied in this connection include trans-1-cyclohexyl-2,3-dibenzoylaziridine (21a), cis-1-cyclohexyl-2,3-dibenzoylaziridine (21b), trans-1-benzyl-2,3-dibenzoylaziridine (22), trans-2-phenyl-3-benzoylaziridine (23) and trans-1,3-dibenzoyl-2-phenylaziridine (24). Laser flash photolysis studies of 21a,b, 22 and 23 and a few other related substrates such as trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1a), cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1b), trans-2-p-anisyl-1-cyclohexyl-3-benzoylaziridine (25), cis-1-cyclohexyl-2-p-tolyl-3-benzoylaziridine (26), and cis-1-cyclohexyl-2-phenyl-

3-p-anisoylaziridine (27) have also been carried out to explore the mechanisms of the observed phototransformations.

Irradiation of the dibenzoylaziridines such as 21a,b in benzene gave the enaminedione 31 as the only isolable product. Similarly, 22, when irradiated in benzene gave the enaminedione 38, along with products such as trans-dibenzoylethylene (36) and benzaldehyde (37). Irradiation of 23, on the other hand, gave a mixture of products such as 37, the dihydropyrazine 44, benzamide (46), acetophenone (47), the pyrazine 48 and 2,5-diphenylpyrazine (49). Irradiation of 24 in benzene gave a mixture of 2,5-diphenyloxazole (17), benzamide (46) and benzoic acid (55).

Nanosecond laser flash photolysis and pulse radiolysis of benzoylaziridines in fluid solutions gave the corresponding azomethine ylide intermediates, characterized by absorptions at longer wavelengths (450-480 nm) through the intermediacy of short-lived carbonyl triplets. The involvement of azomethine ylide intermediates was further confirmed by trapping experiments. Thus, the irradiation of a mixture of 1a and dimethyl acetylenedicarboxylate (DMAD) in acetonitrile, for example, gave a mixture of the pyrroline 57a and the pyrrole 58. Similarly, 1b, under analogous conditions gave the isomeric pyrroline 57b, along with the pyrrole 59b. Irradiation of 21a in acetonitrile in the presence of DMAD gave a mixture of the pyrroline 61 and the pyrrole 63. Similar results were obtained when the irradiation of 21b was carried out in the presence of DMAD. Ketyl-type biradical intermediates formed via intramol-

ecular electron or hydrogen atom transfer, were short lived, except in the case of trans-2-phenyl-3-benzoylaziridine (23). The laser excitation of 23 led to a permanent photoproduct, assigned to the 1,3-butadiene analogue 42, formed through the intermediacy of a relatively long-lived biradical 39.

Chapter III deals with our investigations on the photo-transformations of a few benzopyranol systems containing 1,2-dibenzoylalkene moieties. The substrates that we have studied include 2,3-dibenzoyl-4H-1-benzopyran-4-ol (16a), 2,3-dibenzoyl-4-methyl-4H-1-benzopyran-4-ol (16b), 2,3-dibenzoyl-1H-naphtho[2,1-b]pyran-1-ol (16c), and 2,3-dibenzoyl-2H-1-benzopyran-2-ol (15a). Nanosecond laser flash photolysis studies of 16a-c, 15a and a few other related systems such as 2,3-dibenzoyl-3H-naphtho[2,1-b]pyran-3-ol (15c), 2,3-dibenzoyl-2-methoxy-2H-1-benzopyran (18a), and 2,3-dibenzoyl-3-methoxy-3H-naphtho[2,1-b]pyran (18c) have also been carried out to characterize the nature of the transients involved in these phototransformations.

Irradiation of 16a,c, for example, gave the 2-pyranols 15a,c and their methoxy analogues 18a,c, depending on the solvents employed. However, the irradiation of 16b in solvents such as acetone, benzene and methanol gave exclusively the dehydration product 19b. In the case of 16c, a product such as 22c was also isolated, in addition to 15c, when the irradiation was carried out in benzene. Irradiation of 15a in methanol gave

the methoxy derivative 18a. The formation of the various products in these reactions could be explained through the intermediacy of carbocations 21a-c, produced as a result of photodehydroxylation. Nanosecond laser flash photolysis studies of 15a,c, 16a-c, and 18a,c in benzene or methanol revealed the formation of triplets, characterized by unusually short life-times, which testify to the reactive nature of these triplets. In addition, longer-lived transient species characterized by absorptions at longer wavelengths (700-800 nm) were observed in the cases of 15a,c, which are assigned to bi-radicals produced through triplet-mediated C₂-O bond cleavage.

Reasonable mechanisms have been suggested to account for the formation of the different products in these reactions.

Note: The numbers of the various compounds given here correspond to those given under the respective chapters.

CHAPTER I

PHOTOTRANSFORMATIONS OF EPOXYINDANONE ADDUCTS

I.1 ABSTRACT

Phototransformations of several epoxyindanone adducts such as 6,7-dibenzoyl-8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19a), dimethyl 8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (19b), methyl 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6-carboxylate (19c), 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19d), 8,9-dihydro-5,6,7,8-tetraphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19e), and dimethyl 8,9-dihydro-5-methyl-8-phenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (22) have been investigated by steady-state photolysis, product analysis and laser flash photolysis.

Irradiation of 19a-c in solvents such as acetone, benzene and a mixture (1:9) of benzene and methanol exhibited singlet state-mediated photoisomerizations leading to 2,8-diphenylindeno[1,2-b]furan-4-ones 25a-c in good yields. However, irradiation of 19d and 19e in benzene and in a mixture (1:9) of benzene and methanol exhibited triplet state-mediated reactions leading to the naphthalene derivatives 26d and 26e, respectively, in addition to the singlet state-mediated products 25d and 25e. Under the conditions of workup, both 26d and

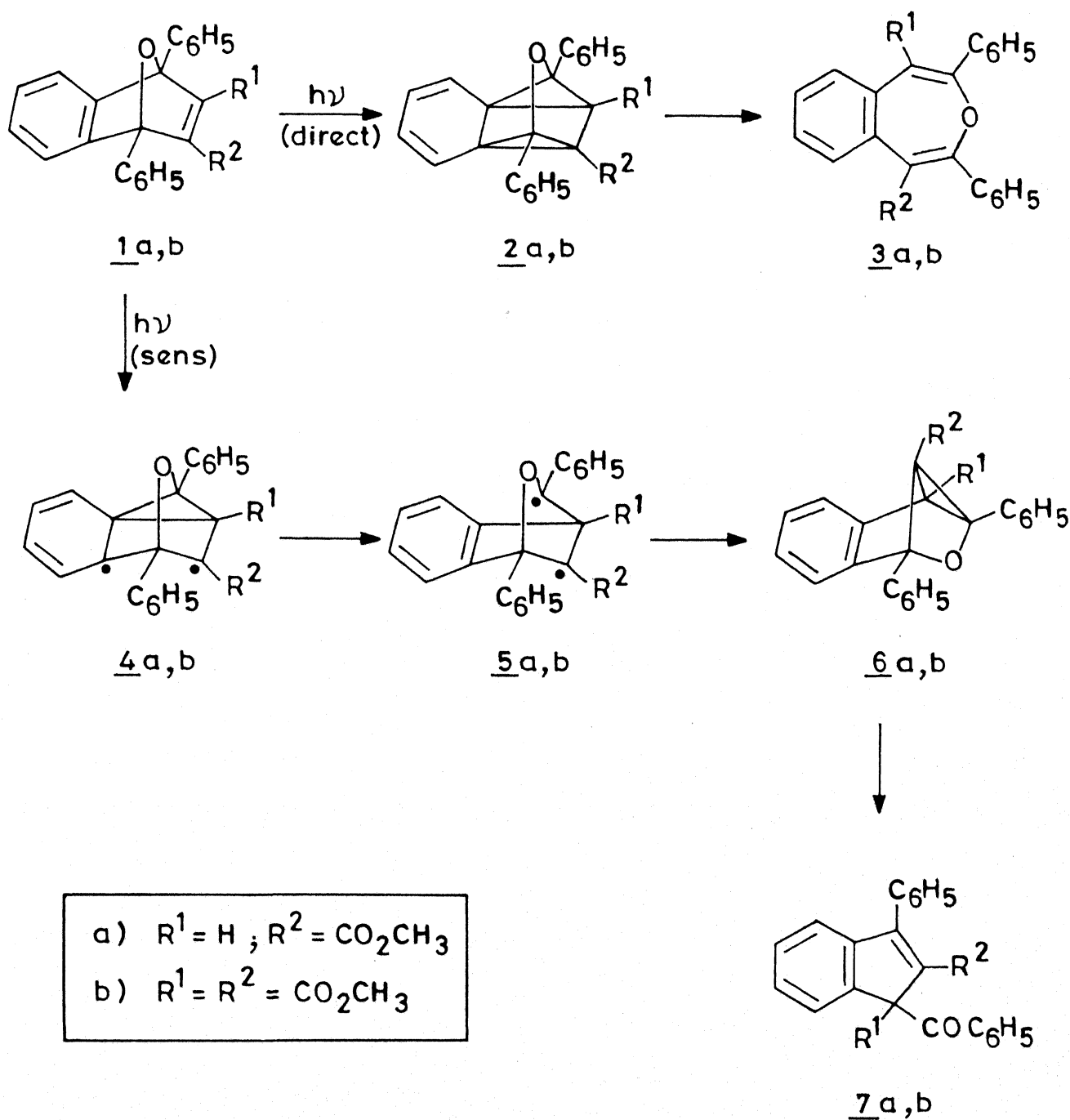
26e were isolated as 27d and 28e, respectively. In contrast, the irradiation of 19d in acetone gave mostly 27d. Interestingly, the formation of 27d was completely suppressed, when the irradiation of 19d was carried out in air-saturated benzene. Irradiation of 22 in acetone, benzene and in methanol gave the naphthalene derivative 32, in moderate yields, most probably via singlet mediated pathways.

Reasonable mechanisms for the formation of the different products in these reactions have been suggested. Nanosecond laser pulse excitation of 19a-e gave transient absorptions, tentatively assigned to biradicals from Norrish type I photocleavage. In some cases, triplets acting as precursors for the di- π -methane rearrangements to naphthalene derivatives, have been observed under energy-transfer sensitization.

I.2 INTRODUCTION

Photochemical transformations of several 1,4- and 1,2-epoxy compounds containing carbonyl substituents have been reported in the literature.¹⁻⁸ Thus, it has been observed that the direct irradiation of the benzoxanorbornadienes 1a,b, for example, leads to the corresponding oxaquadricyclanes 2a,b, presumably through a [$\pi^2S + \pi^2S$] type of addition. In contrast, the sensitized irradiation of 1a,b leads to the formation of the corresponding indene derivatives 7a,b (Scheme I.1).⁷ It has been suggested that the initially formed triplet state intermediates in these cases undergo transformation to the

Scheme 1.1

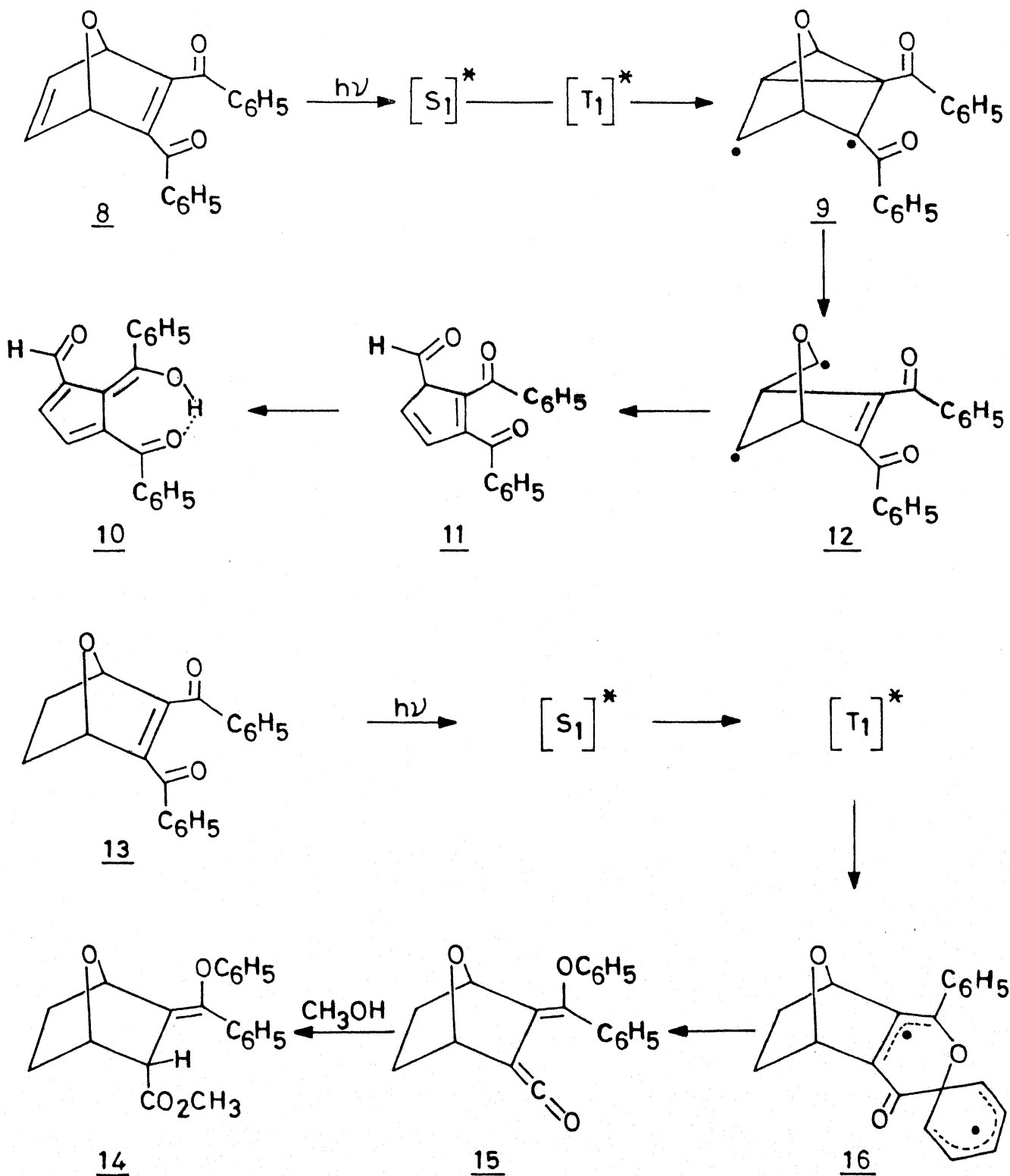


corresponding tetracyclic intermediates 6a,b, through the biradical intermediates 4a,b and 5a,b. Subsequent rearrangement of 6a,b will lead to the observed products 7a,b.

Phototransformations of several 1,4-epoxy compounds containing 1,2-dibenzoylalkene moieties have been reported earlier from this laboratory.⁸ It has been observed that these substrates undergo transformation in two distinct pathways - one involving the reaction of the 1,4-epoxy component and the other related to the rearrangement of the 1,2-dibenzoylalkene component. Thus, the irradiation of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (8) in benzene, for example, gave the cyclopentadiene derivative 10, involving the reaction of the 1,4-epoxy component (Scheme I.2). Interestingly, the irradiation of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (13) in methanol, on the other hand gave the ester 14, involving the 1,2-dibenzoylalkene component, as shown in Scheme I.2.

In the present investigation, we have examined the phototransformations of a few epoxyindanone adducts with a view to understand the nature of the products formed in these reactions and also to characterize the transients involved in these reactions, through laser flash photolysis studies. The substrates that we have examined in this connection include, 6,7-dibenzoyl-8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19a), dimethyl 8,9-dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (19b), methyl 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclo-

Scheme 1.2

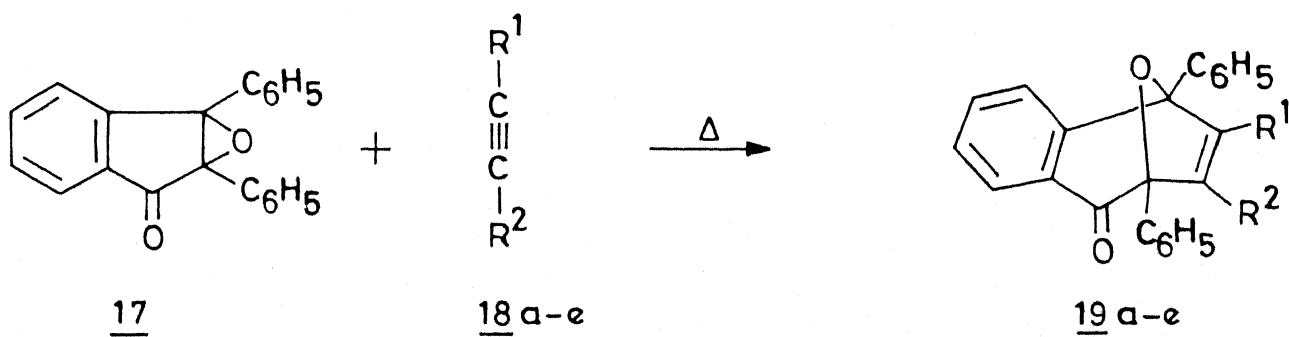


hepten-9-one-6-carboxylate (19c), 8,9-dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19d), 8,9-dihydro-5,6,7,8-tetraphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19e), and dimethyl 8,9-dihydro-5-methyl-8-phenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (22). Examination of the structural features of these substrates reveals that they are multichromophoric systems and therefore should be capable of undergoing different types of photoreactions such as the Norrish type I photocleavage, the di- π -methane rearrangement⁹ and the 1,2-dibenzoylalkene rearrangement.¹⁰⁻¹³

I.3 RESULTS AND DISCUSSION

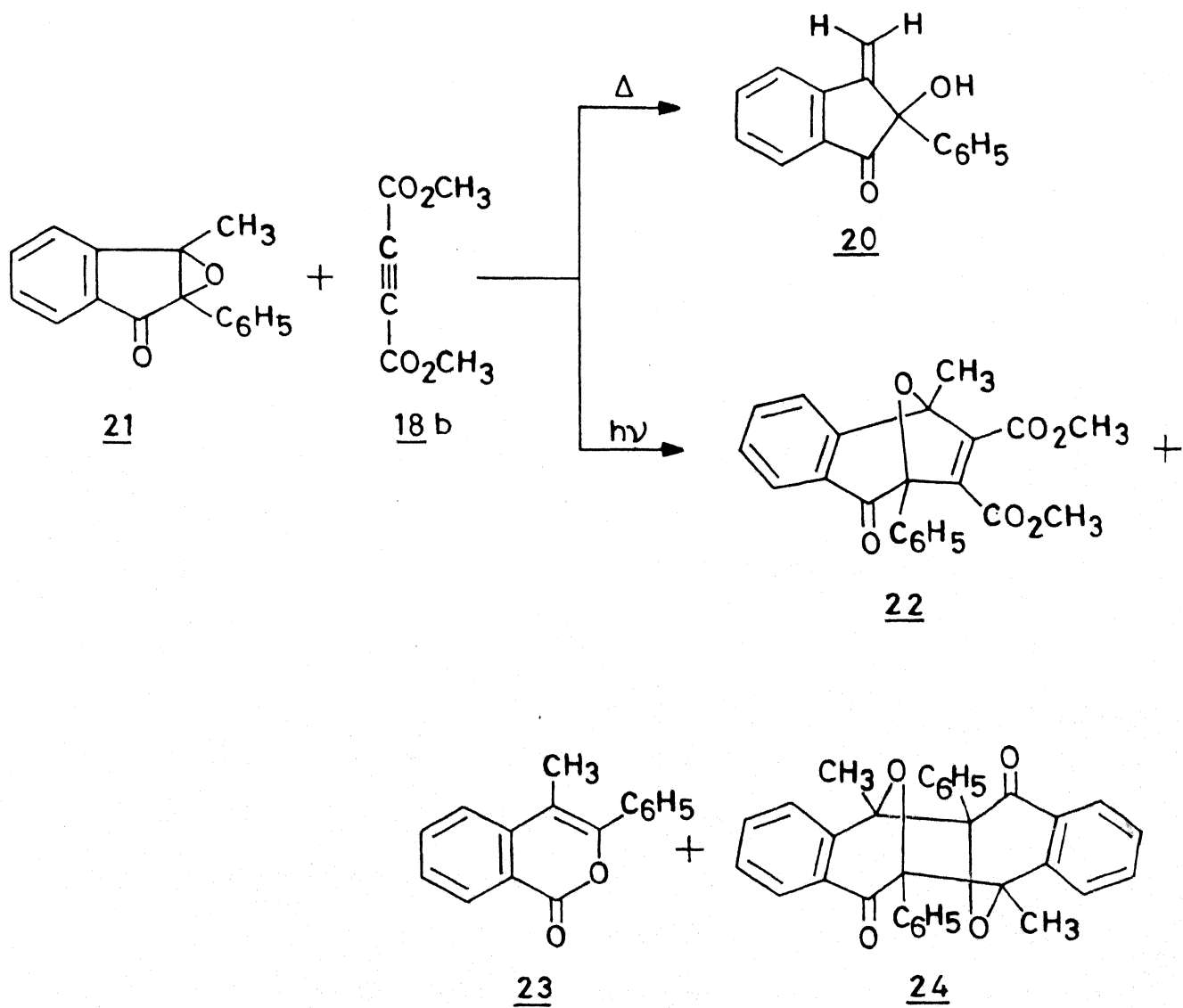
I.3.1 Preparation of Starting Materials. The epoxy-indanone adducts 19a-e were prepared in yields ranging between 69-95% through the thermal addition of the carbonyl ylide formed from 2,3-diphenyl-2,3-epoxy-1-indanone (17) with the appropriate dipolarophiles (18a-e) (Scheme I.3). The epoxyindanone 21, however, did not give the adduct 22 under thermal conditions. Subsequently, we observed that the adduct 22 could be prepared in moderate yields from 21 under photochemical conditions. Minor amounts of other products such as the isocoumarin 23 and the dimer 24 were also formed under these conditions. (Scheme I.4, see also the experimental section). Of these adducts, 19b¹⁴ and 19e¹⁵ were reported earlier. The structures of the adducts 19a, 19c, 19d and 22 and the dimeric species 24 were established on the basis of analytical results, spectral data and literature

Scheme 1.3



- a) $\text{R}^1 = \text{R}^2 = \text{COC}_6\text{H}_5$
- b) $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{CH}_3$
- c) $\text{R}^1 = \text{CO}_2\text{CH}_3$; $\text{R}^2 = \text{C}_6\text{H}_5$
- d) $\text{R}^1 = \text{H}$; $\text{R}^2 = \text{C}_6\text{H}_5$
- e) $\text{R}^1 = \text{R}^2 = \text{C}_6\text{H}_5$

Scheme 1.4



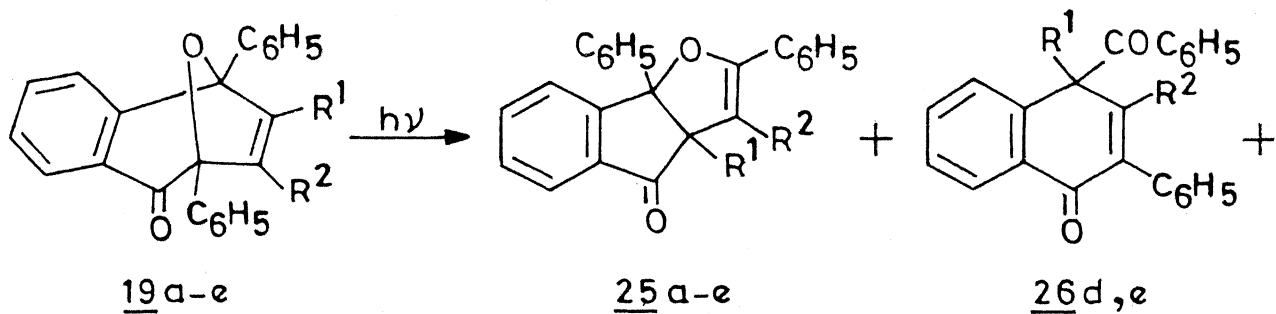
precedents.¹⁴⁻²⁷

I.3.2 Preparative Photochemistry and Product Identification. Irradiation (RPR, 3000 Å) of an acetone solution of 19a gave a 33% yield of an isomeric product, identified as 3,3a-dibenzoyl-3a,8b-dihydro-2,8b-diphenylindeno[1,2-b]furan-4-one (25a) (Scheme I.5). Similar results were obtained when the irradiation of 19a was carried out in benzene and in a mixture (1:9) of benzene and methanol. The structure of 25a was established on the basis of analytical results, spectral evidence and chemical transformations. Treatment of 25a with sodium methoxide in methanol, for example, gave the enol-ester 29a (70%), which could be acetylated by treatment with acetic anhydride to give the ester 30a (42%). Similar hydrolysis of indenone derivatives have been reported earlier in the literature.²⁸ Further confirmation of the structure of 25a was obtained through X-ray crystallographic analysis. Figure I.1 shows the computer-generated drawing of the structure of 25a.

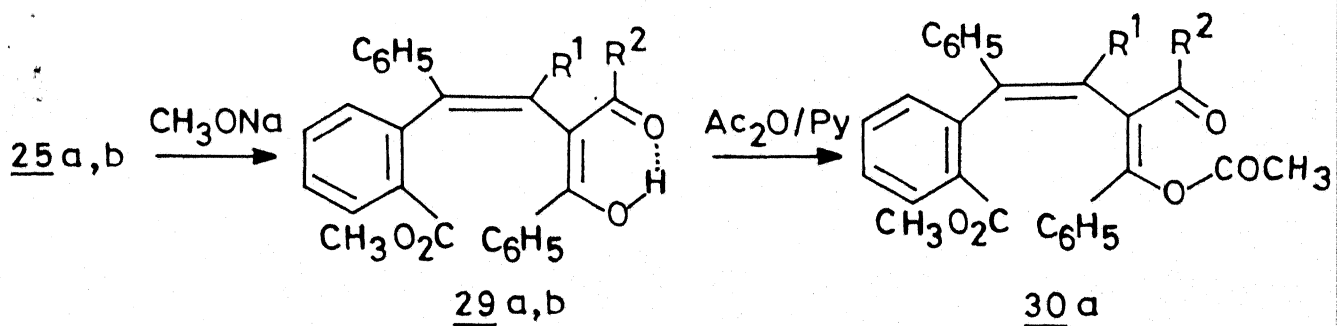
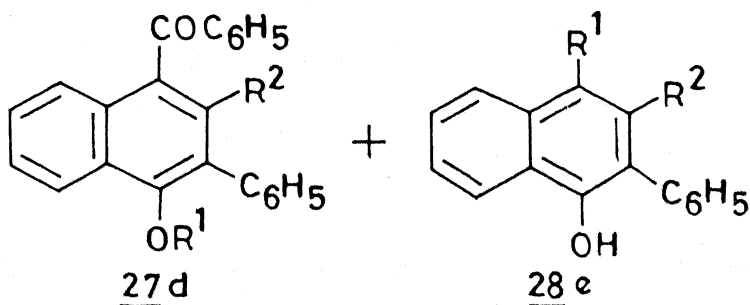
Similarly, the irradiation of 19b in acetone, benzene and in a mixture (1:9) of benzene and methanol gave the rearranged product 25b (60-77%). Treatment of 25b with sodium methoxide in tetrahydrofuran (THF) gave the enol-ester 29b (56%) (Scheme I.5). Likewise, the irradiation of 19c in acetone, benzene or in a mixture (1:9) of benzene and methanol gave the corresponding rearranged product 25c (55-80%).

Irradiation of 19d in benzene, on the other hand, gave a mixture of the tricyclic compound 25d (43%) and the naphthalene

Scheme 1.5



- a) $R^1 = R^2 = COC_6H_5$
 b) $R^1 = R^2 = CO_2CH_3$
 c) $R^1 = CO_2CH_3; R^2 = C_6H_5$
 d) $R^1 = H; R^2 = C_6H_5$
 e) $R^1 = R^2 = C_6H_5$



- a) $R^1 = COC_6H_5; R^2 = C_6H_5$
 b) $R^1 = CO_2CH_3; R^2 = OCH_3$

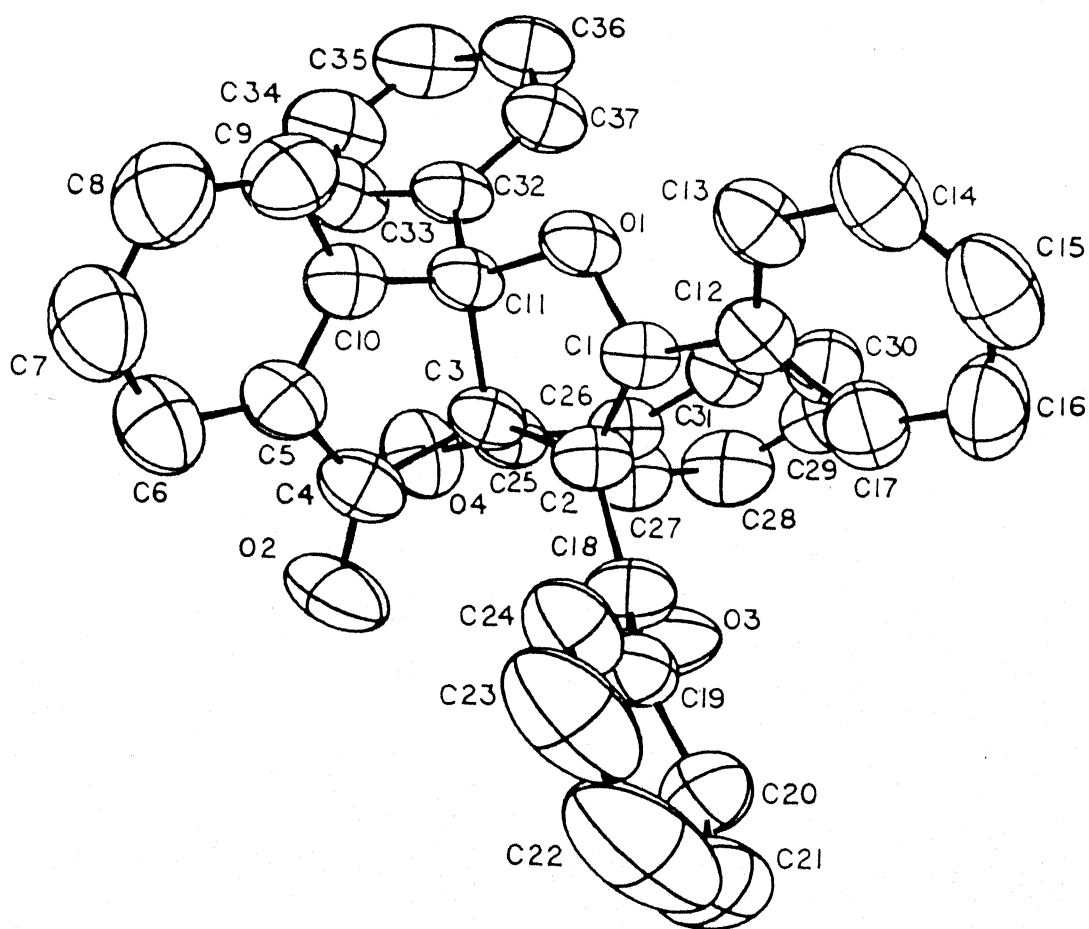
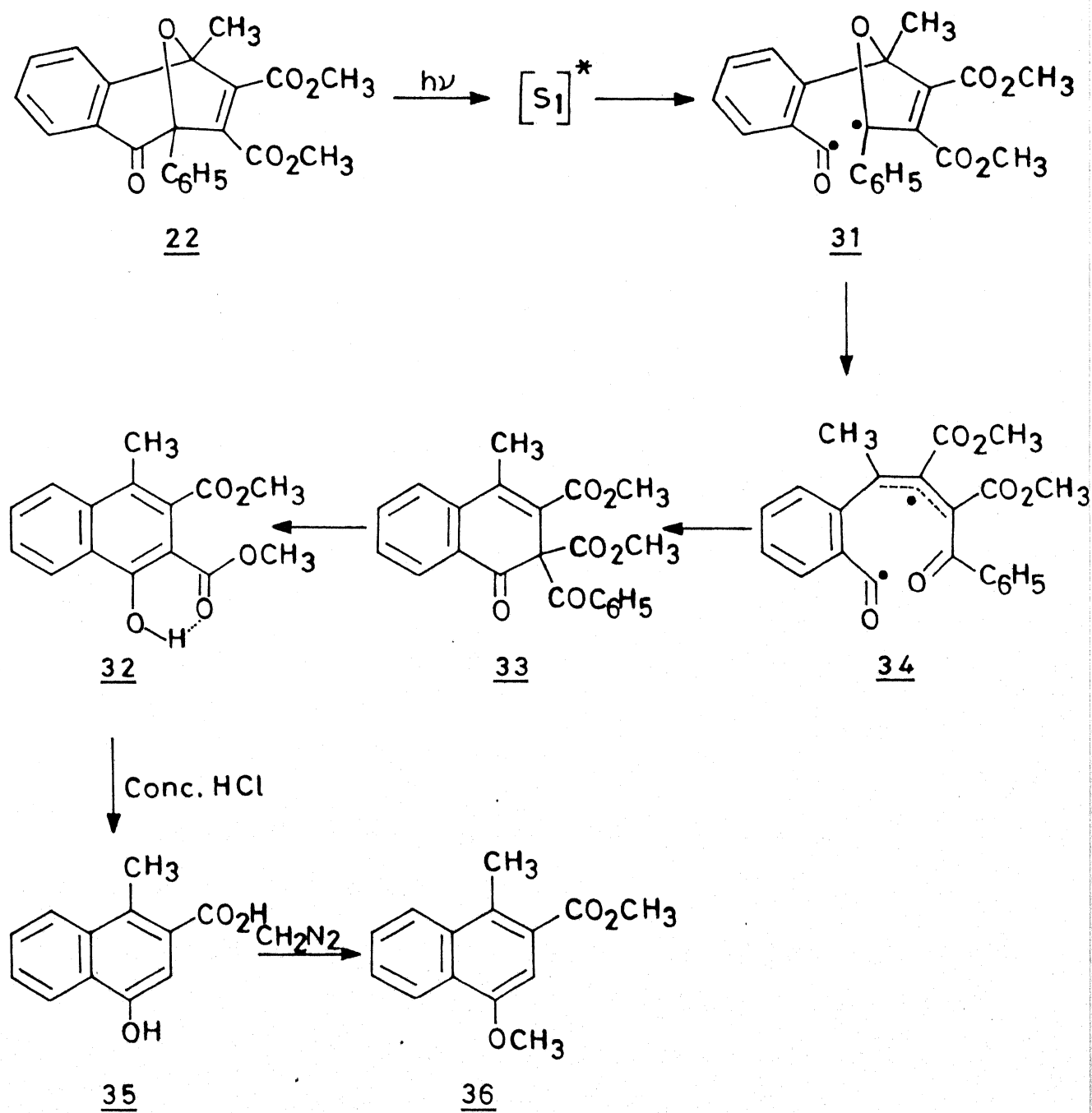


Fig. I.1 Computer-generated drawing of 25a derived from the X-ray coordinates with hydrogens omitted for clarity.

derivative 27d (17%), along with a 30% recovery of the unchanged 19d. Similarly, the irradiation of 19d in a mixture (1:9) of benzene and methanol gave a mixture of 25d (36%), 27d (13%), and the unchanged 19d (22%). In contrast, the irradiation of 19d in acetone gave a 80% yield of 27d, along with a small amount (5%) of 25d. Interestingly, the irradiation of 19d in air-saturated benzene gave 25d (33%) as the only isolable product, along with substantial amounts (55%) of the unchanged starting material (19d) (Scheme I.5).

Irradiation of 19e in acetone gave a mixture of the tricyclic compound 25e (35%), 4-benzoyl-2,3,4-triphenyl-4H-1-naphthone (26e, 25%), and 2,3,4-triphenyl-1-naphthol (28e, 15%). Similarly, the irradiation of 19e in benzene and in a mixture (1:9) of benzene and methanol gave a mixture of 25e (30-33%), 26e (5-10%), 28e (7-25%), and some unchanged 19e (15-25%), in each case. The structures of all the photoproducts were established on the basis of analytical results, spectral data and chemical evidence. Treatment of 26e with aluminium chloride in methylene chloride, for example, gave a 64% yield of 28e.^{7,29}

Irradiation of an acetone solution of 22 gave a 35% yield of a product, identified as dimethyl 4-methyl-1-naphthol-2,3-dicarboxylate (32), along with a 60% recovery of the unchanged starting material (22) (Scheme I.6). Similarly, the irradiation of 22 in benzene and in methanol gave a mixture of 32 (14-17%) and some unchanged 22 (65-82%), in each case. The

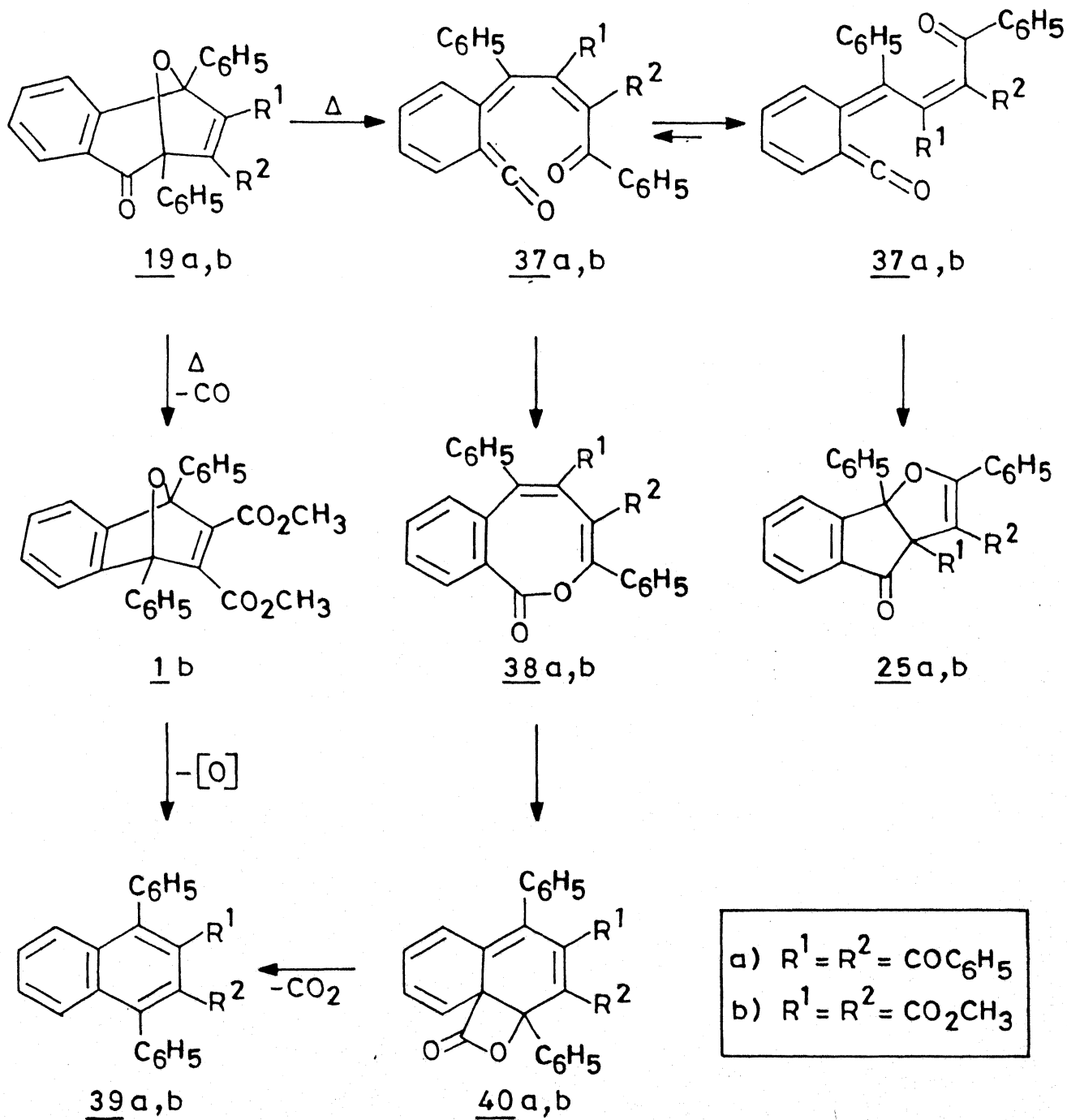
Scheme 1.6

structure of the naphthol product 32 was confirmed through analytical results, spectral data and chemical evidence. Thus, treatment of 32 with concentrated hydrochloric acid, for example, gave the naphthoic acid derivative 35 (47%), which could be further transformed to 36, in a 63% yield by treatment with diazomethane as shown in Scheme I.6.^{30,31}

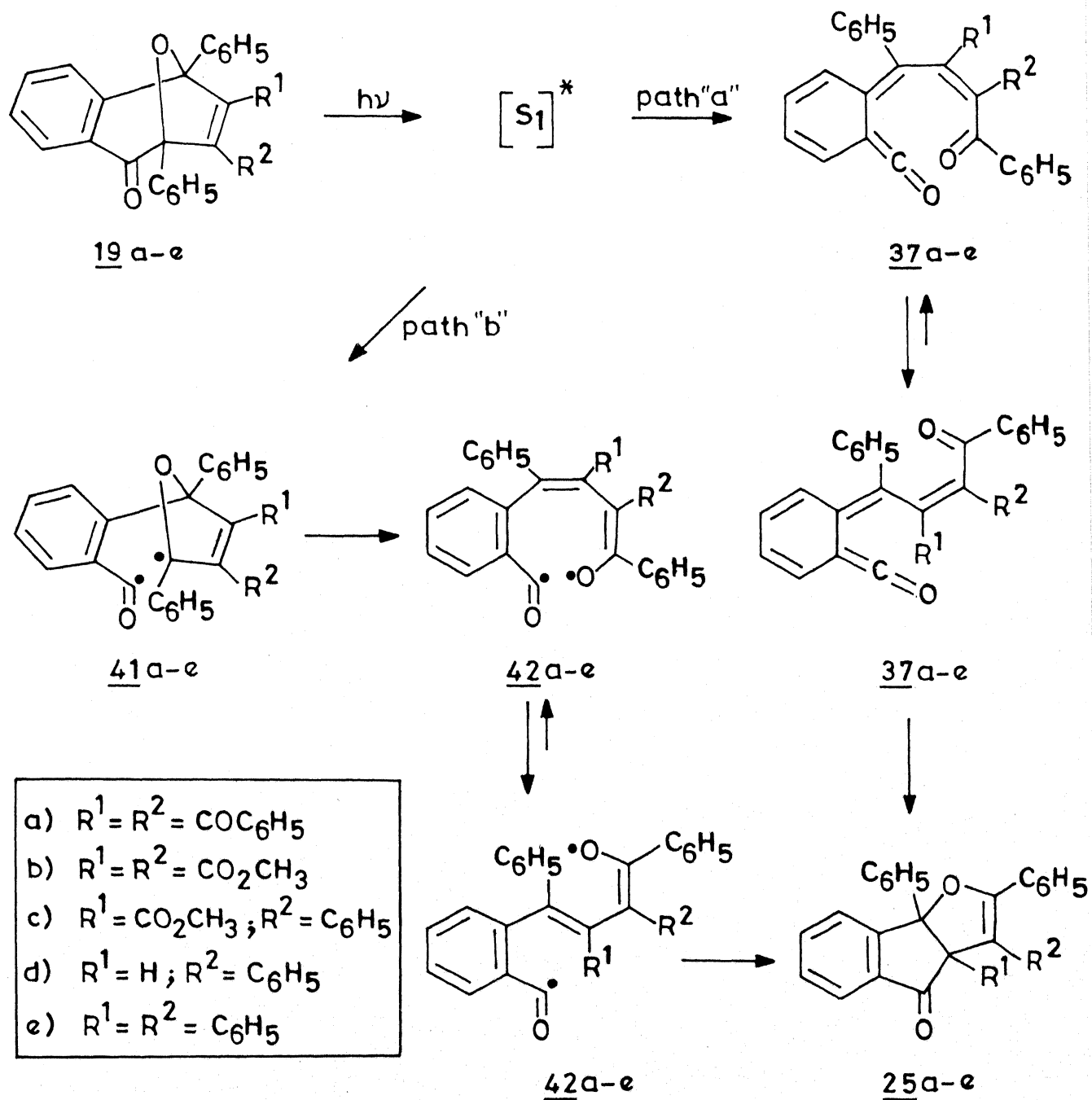
I.3.3 Thermal Transformations of 19a and 19b. Thermolysis of 19a at ca. 300-310 °C for 3 h in a sealed tube gave a 25% yield of the rearranged product 25a and a small amount of 2,3-dibenzoyl-1,4-diphenylnaphthalene (39a, 5%), along with a 32% recovery of the unchanged starting material (19a) (Scheme I.7). Similarly, neat heating of 19b at ca. 290-295 °C for 1.5 h gave a mixture of 25b (7%), dimethyl 1,4-diphenylnaphthalene-2,3-dicarboxylate (39b, 3%), the epoxynaphthalene derivative 1b (2%), and the unchanged starting material (19b, 52%). When 19b was heated at ca. 290-295 °C for a longer period (3 h), better yields of 25b (20%) and 39b (35%) were obtained (Scheme I.7).

I.3.4 Discussion. The formation of the different products in the phototransformations of 19a-e could be understood in terms of the pathways shown in Schemes I.8 and I.9. Apriori, the rearranged products 25a-e could arise through a singlet state mediated pathway, involving the ketene intermediates 37a-e (path 'a') or alternatively, through the singlet biradical intermediates 41a-e and 42a-e (path 'b'), as shown in Scheme I.8. Mention may be made here that benzoxocinones 38

Scheme 1.7

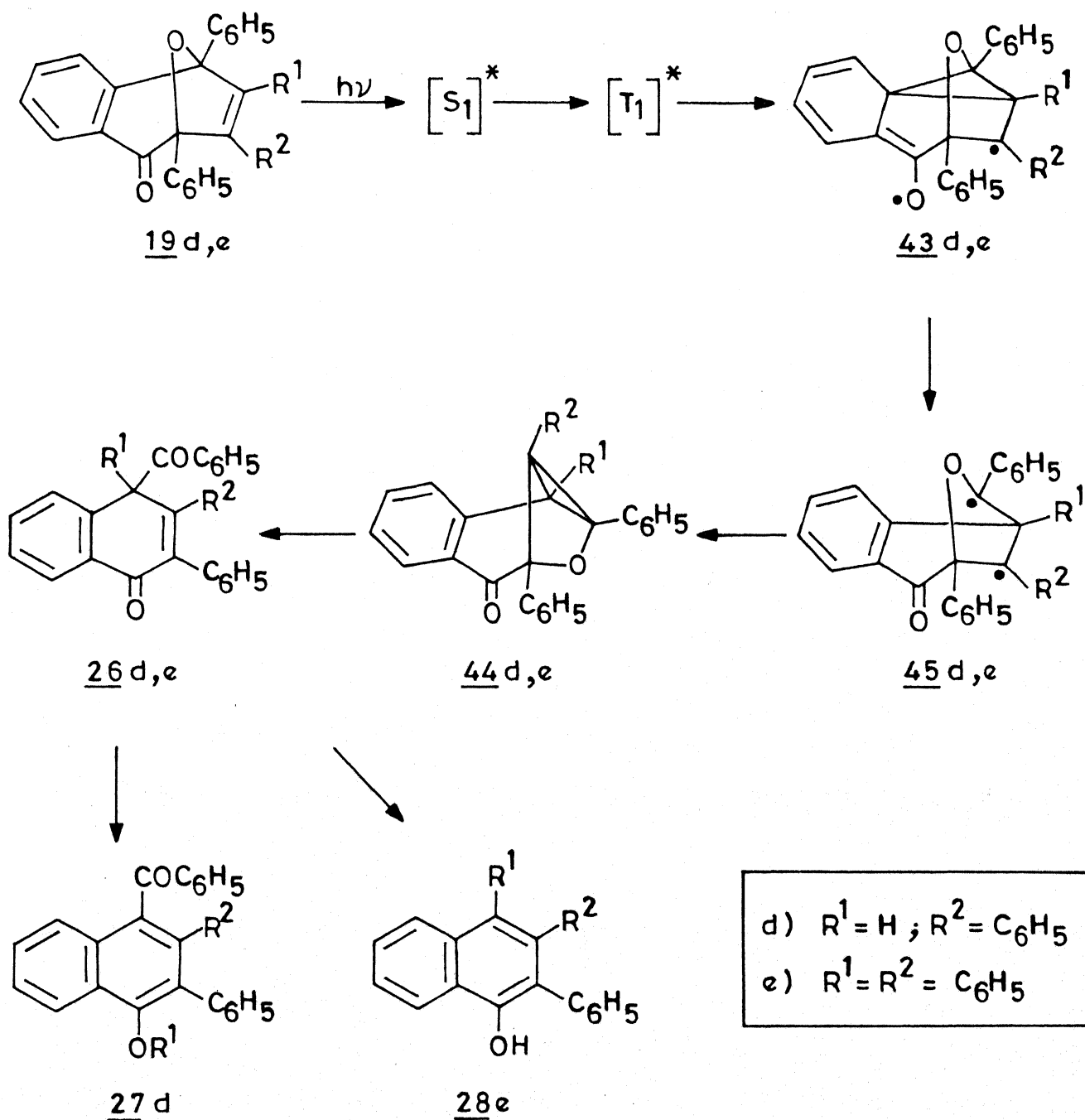


Scheme 1.8



(Scheme I.7), which could be formed by the cyclization of ketene intermediates 37a-e or the biradical intermediates 42a-e were not isolated in these reactions. Also, no ketene derived addition products, such as acids or esters could be isolated when the irradiation of 19a-e was carried out in a mixture (1:9) of benzene and methanol. This would suggest that either the ketene intermediates 37a-e are not involved in these reactions or they undergo rapid electrocyclic ring-closure to give the corresponding cyclized products, 25a-e. The formation of the naphthalene derivatives 26d,e in the reactions of 19d,e, however, can be explained in terms of a di- π -methane rearrangement (Zimmerman rearrangement),⁹ proceeding through the triplet excited state, as shown in Scheme I.9. The triplet excited states of 19d,e, for example, can rearrange to the tetracyclic oxetane derivatives 44d,e, through the biradical intermediates 43d,e and 45d,e, respectively. Further transformation of 44d,e will lead to the naphthones 26d,e. Direct conversion of 45d,e to 26d,e is also a feasible pathway. The formation of the observed products such as 27d from 26d could be understood in terms of a prototropic shift, whereas 28e may arise through a hydrolytic cleavage of 26e. The fact that acetone-sensitized irradiation of 19d gave 27d in high yields and also that the irradiation of 19d in air-saturated benzene totally suppressed the formation of 27d, supports the assumption that triplet state mediated pathways are involved in these transformations (Scheme I.9).

Scheme 1.9



It is pertinent to note that singlet state mediated pathways, leading to the rearrangement products 25a-c are exclusively followed in the phototransformation of the epoxy-indanone adducts 19a-c, containing keto and ester moieties attached to the olefinic double bond. In contrast, the phototransformations of 19d and 19e, proceed through both singlet and triplet state mediated pathways. It is likely that the keto and ester groups present in the adducts 19a-c may be facilitating the singlet biradical pathway (path 'b'), as shown in Scheme I.8.

The formation of the naphthalene derivative 32 from 22 could be understood in terms of the pathways shown in Scheme I.6. The singlet excited state of 22, for example, can undergo a Norrish Type I cleavage leading to the biradical 31, which can subsequently be transformed to the naphthone derivative 33, through 34. Hydrolytic cleavage of 33, under the conditions of workup, will lead to the observed product 32. In an analogous phototransformation of benzazocines to naphthalene derivatives, Padwa *et al.*^{32,33} have proposed the intermediacy of ketene derivatives and such a possibility cannot be ruled out completely in this case. However, it may be pointed out that no ketene derived products could be isolated when the irradiation of 22 was carried out in methanol.

The formation of the various products in the thermal transformations of 19a and 19b can be explained in terms of the pathways shown in Scheme I.7. The formation of the

rearranged products 25a,b may be occurring through the ketene intermediates 37a,b and the involvement of such ketene intermediates in analogous thermal transformations has been reported in the literature.^{15,16} However, the alternative pathway involving biradical intermediates cannot also be ruled out in these cases. The formation of small amounts of the epoxynaphthalene 1b from 19b may proceed through the decarbonylation of the biradical intermediate 41 (Scheme I.8, path 'b'), followed by recombination, whereas 39b may arise through the deoxygenation of 1b. In support of this assumption, we have shown that the neat heating of 1b at ca. 290-295 °C for 2 h gives a 56% yield of 39b. Similar deoxygenation reactions of 1,4-epoxy compounds have been reported in the literature.³⁴ An alternate pathway for the formation of 39a,b from 19a,b may be through the decarboxylation of the tricyclic intermediates 40a,b, which could be formed from benzoxacinone intermediates 38a,b (Scheme I.7). The benzoxacinone intermediates 38a,b, in turn, could be formed through the electrocyclic ring closure of the ketene intermediates 37a,b. It may be mentioned in this connection that a similar mechanism has been proposed in the formation of dimethyl 2,5,6-triphenylpyridine-3,4-dicarboxylate through the reaction of 2,4,5-triphenyl-3H-pyrrole-3-one-1-oxide with dimethyl acetylenedicarboxylate^{35,36} and also in the thermal transformation of dimethyl 4-oxo-1,3,5-triphenyl-8-oxabicyclo[3.2.1]octa-2,6-diene-6,7-dicarboxylate, leading to the formation of dimethyl 3,4,6-triphenylphthalate.³⁷

I.3.5 Laser Flash Photolysis Studies.³⁸ In order to obtain information on the photointermediates, namely, triplets, biradicals and ketenes that can plausibly be involved in the observed phototransformations (Scheme I.8 and Scheme I.9), the substrates 19a-e were subjected to laser flash photolysis investigations in benzene and methanol solutions at room temperature. Upon 337.1 nm laser pulse excitation, deaerated benzene solutions of 19a-e give rise to weak absorbance changes³⁹ at 350-500 nm (Figure I.2), which showed very little or no decay on the longest time scale ($\sim 100 \mu\text{s}$) used in our experiments. Oxygen ($\sim 2 \text{ mM}$) did not affect the yields or decay kinetics of the long-lived photoproducts. The insensitivity of transient decay towards oxygen as well as ferrocene (5 mM) rules out assignments of the long-lived absorbance changes in terms of the triplets of 19a-e. On adding methanol (up to 8 mM) to benzene solutions, the decay of photoproducts remains practically unchanged. This coupled with the fact that products assignable to the trapping of ketene intermediates 37a-e were not obtained in the course of steady-state photolysis of 19a-e in benzene-methanol mixtures suggests that the laser-induced long-lived absorbance changes cannot possibly be due to the ketene intermediates 37a-e (Scheme I.8). Thus, we are left with assignments in terms of the biradicals 41, 42, 43 and 45 and/or the final products, 25a-e (Scheme I.8 and Scheme I.9). The involvement of biradicals 43 and 45 can be ruled out in the case of 19a-c

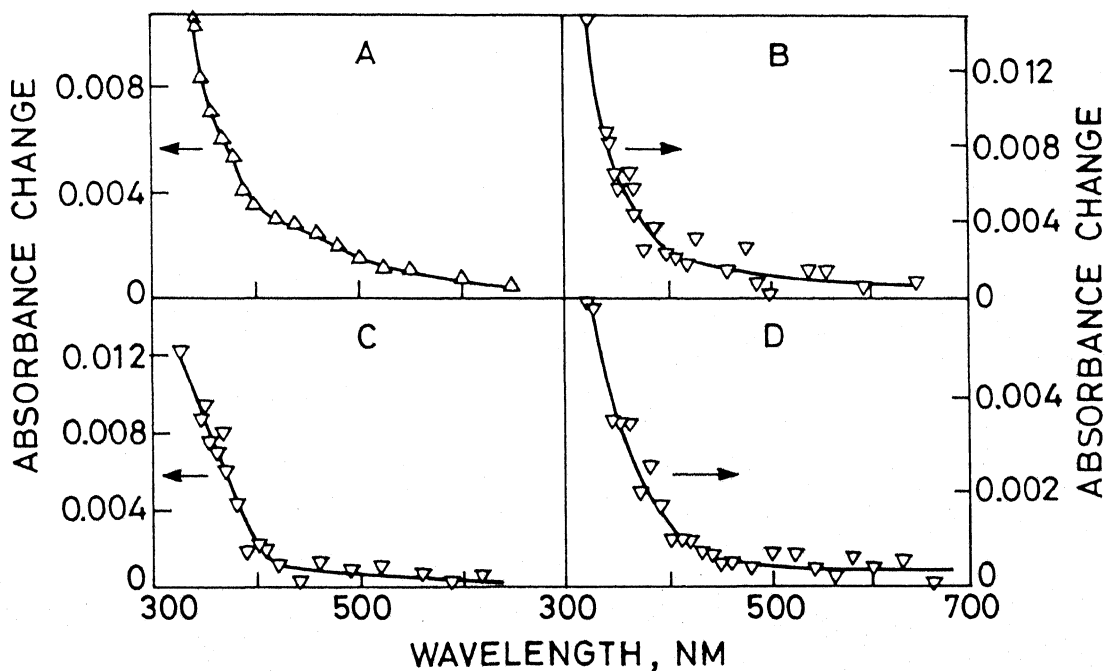


Fig. 1.2 Absorbance changes at 5-10 μ s following 337.1 nm laser flash photolysis of (A) 19a, (B) 19c, (C) 19d and (D) 19e in deaerated benzene. Ground-state absorbances of the substrates at 337.1 nm were 0.5-1.0 (in 2 mm cells)

because photoproducts mediated through them are not isolated from the photolysates of these substrates. Also, the ground-state absorption spectra of the photoproducts 25a-e indicate that they do not absorb significantly at wavelengths longer than 400 nm. Based on the fact that the formation of 25a-e is the major phototransformation observed with all the substrates 19a-e and that the absorbance changes caused by laser pulse excitation extend well beyond 400 nm (Figure I.2), it seems plausible that the latter are, at least in part, due to the biradicals 41 and 42. Since we have not explored the decay behaviour of the laser induced absorptions on time scales longer than microsecond and since there is a possibility that some minor photoproducts have remained undetected in the course of isolation and analysis, the biradical assignment is to be considered tentative.

In order to see if triplets capable of transferring energy to 1-methylnaphthalene (MN) are produced as a result of photoexcitation of 19a-e, these were flash photolysed at 337.1 nm in benzene solutions in the presence of high concentrations of MN. In the case of 19a and 19d, no significant transient absorption that could be attributed to energy transfer derived MN triplet ($\lambda_{\text{max}}^T = 425 \text{ nm}$) was observed at the highest [MN] (0.6 M). For 19b,c,e, small, but nonnegligible absorptions due to $^3\text{MN}^*$ were noted at high [MN] (0.2-0.6 M). The intercept-to-slope ratios of the plots of reciprocal of transient absorbances (end-of-pulse) due to $^3\text{MN}^*$

against $1/[MN]$ were 2, 7 and 2 M^{-1} for 19b, 19c, and 19e, respectively. These represent $k_q^T \tau_T$ values, where k_q^T is the bimolecular rate constant for energy transfer from a donor triplet state of lifetime τ_T . The low $k_q^T \tau_T$ values suggest that the donor triplets are short-lived ($\tau_T \leq 1 \text{ ns}$ if the energy transfer is diffusion-controlled, e.g., from a carbonyl-like triplet) and/or the energy transfer process is very slow.

Several experiments were done in which benzophenone or p-methoxyacetophenone were preferentially excited by laser pulses ($\lambda_{\text{max}} = 337.1$ or 355 nm) in the presence of $0.5\text{--}2 \text{ mM}$ of 19a-e in benzene. In these experiments, the aromatic ketones were meant to act as donors of triplet excitation to the substrates. Their ground-state absorbances at the laser wavelengths were kept high ($2.0\text{--}3.0$ in 2 mm cells) and the fraction of laser photons absorbed by the substrates (acceptors) were usually small ($\leq 10\%$). The bimolecular rate constants for benzophenone triplet quenching by 20a-e were $1.5\text{--}3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene. Only in the case of 19c and 19e did we observe fairly long-lived transients, produced via the route of triplet excitation transfer. The absorption spectra of these transients are shown in Figure I.3. While in the case of 19e two maxima (370 and 530 nm) are clearly discernible in the spectral region $>360 \text{ nm}$, the transient from 19c displays its major maximum at $<360 \text{ nm}$.⁴⁰ The triplet-mediated transient from 19c decays by first-order

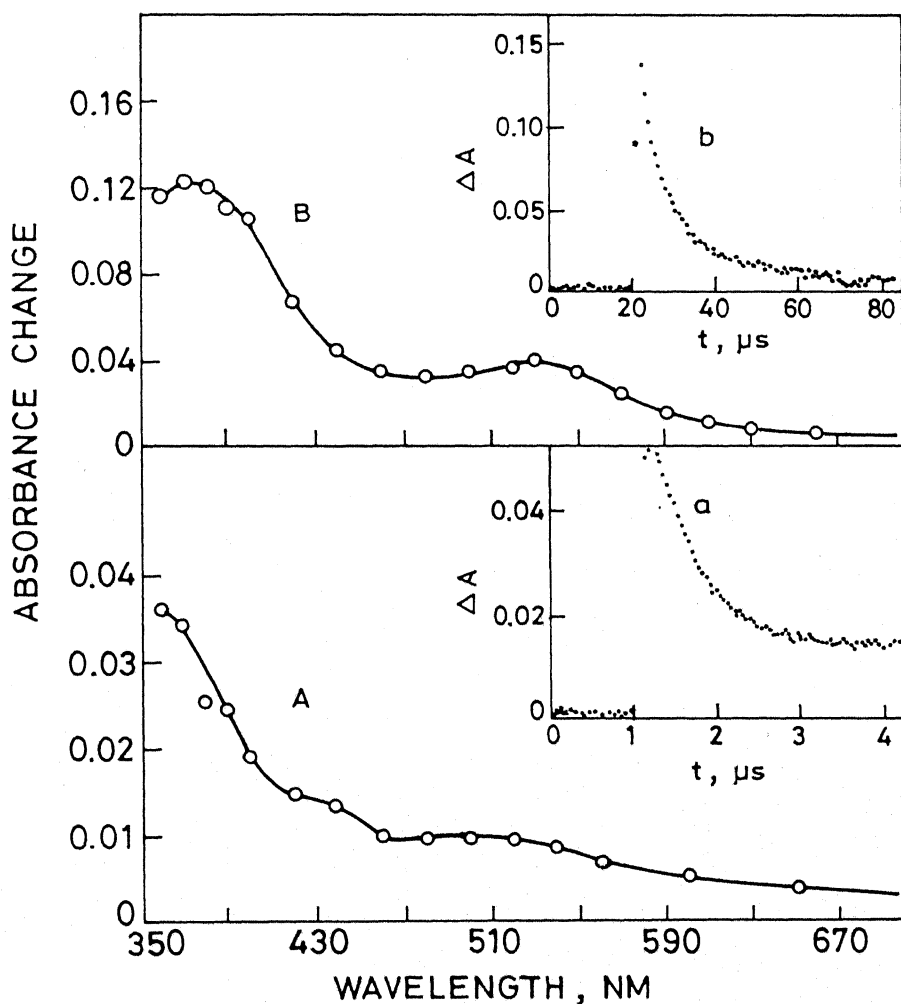


Fig. 1.3 Transient absorption at 1 μs following 337.1 nm laser flash photolysis of benzophenone in the presence of (A) 1.3 mM **19c** and (B) 1.1 mM **19e** in degassed benzene. Insets: kinetic traces showing the decay of triplet-derived transients at 370 nm in the case of (a) **19c** and (b) **19e** (substrate concentration = 5 mM for both).

kinetics with a lifetime of 540 ns (measured at 5 mM [19c], see inset a of Figure I.3). The decay of 370/530 nm transient derived from 19e is complex and takes place on a longer time scale ($\tau_{1/2} \sim 11 \mu\text{s}$, see inset b of Figure I.3).

Oxygen and ferrocene readily enhance the decay of the triplet derived transients in the case of 19c and 19e. The rate constants for quenching by oxygen are 7.8×10^8 and $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in the case of 19c and 19e, respectively. This quenching behaviour suggests a triplet assignment in both the cases. However, we find it interesting that the triplet of 19e is only poorly quenched by ferrocene. In the absence of geometric relaxation or intramolecular interaction, the energy of the lowest triplet of 19e should be comparable to that of cis-stilbene ($E_T \simeq 57 \text{ kcal mol}^{-1}$)^{41,42} and energy transfer from it to ferrocene ($E_T \simeq 40 \text{ kcal mol}^{-1}$)⁴³ should be highly exothermic. Although the cis-stilbene moiety of 19e has a scope for undergoing partial distortion in the triplet state, that this distortion is not pronounced is indicated by the long lifetime of the observed triplet. It is plausible that the intramolecular interaction of the cis-stilbene moiety with the aromatic carbonyl chromophore, expressed in terms of the biradical structures 43 and 45 results in substantial lowering of the triplet energy. Alternatively, the triplet is in fast equilibrium with the biradicals, the latter being nonquenchable by ferrocene. Similar triplet quenching behaviors have been reported⁴⁴ for several dibenzo-

barrelene systems which undergo triplet mediated di- π -methane rearrangement to dibenzosemibullvalenes.

While the lack of observation of a triplet on our time scale in the case of 19b and 19d can be understood in terms of short lifetimes and/or weak absorptions at >360 nm, the same in the case of 19a is surprising. It appears that the lowest triplet of 19a is short-lived (<100 ns)⁴⁵ because of intramolecular photochemistry (absorbance changes due to long-lived photoproducts, similar to those produced under direct laser excitation, are also observed under triplet sensitization). By the same token, although the molecule has the dibenzoylalkene moiety locked in a cis-geometry, it does not undergo the well-known intramolecular phenyl group migration.¹⁰⁻¹² Besides the lack of isolation of 2-butenic acid/ester derivatives from the steady-state photolysis of 19a, we do not observe, in the laser flash photolysis of 19a in alcohol-containing solvents, the growth of transient absorptions assignable to the addition of alcohol to ketene intermediates. The latter is a characteristic behaviour^{46,47} of cis-1,2-dibenzoylalkene systems that undergo the rearrangement (singlet-mediated) with high yields. Again, the absence of this reaction in the case of 19a is indicative of unfavourable competition with fast physiochemical pathways (i.e., path 'a' and path 'b' in Scheme I.8).

I.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on either Perkin-Elmer Model 377 or 580 infrared spectrometers. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. The ^1H NMR spectra were recorded on either Varian EM-390 or HA-100 NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a JEOL JMS-D 300 mass spectrometer at 70 eV. All steady-state irradiations were carried out in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR 2537 or 3000 Å) in quartz tubes.

I.4.1 Starting Materials. 2,3-Diphenyl-2,3-epoxy-1-indanone (17),⁴⁸ mp 139-140 °C, dibenzoylacetylene (DBA, 18a),^{49,50} mp 110-111 °C, dimethyl acetylenedicarboxylate (DMAD, 18b),⁵¹ bp 95-98 °C (19 mm), methyl phenylpropiolate (18c),⁵² bp 70-75 °C (20 mm), phenylacetylene (18d),⁵³ bp 82-83 °C (80 mm), diphenylacetylene (18e),⁵⁴ mp 59-60 °C, and the epoxyindanone adducts 19b,¹⁴ mp 168-169 °C and 19e,¹⁵ mp 170-171 °C were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

I.4.2 Preparation of the Epoxyindanone Adducts 19a,c,d.

A general procedure was to reflux a mixture of 17 (10 mmol) and the appropriate dipolarophile (18a,c,d, 10 mmol) in o-dichlorobenzene (10 mL, bp 175-178 °C) for 30 minutes. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (1:9) of benzene and petroleum ether gave the corresponding adducts.

6,7-Dibenzoyl-8,9-dihydro-5,8-diphenyl-5H-5,8-epoxy-benzocyclohepten-9-one (19a). 19a was obtained in a 92% yield, mp 205-206 °C.

IR spectrum ν_{\max} (KBr): 3060, 3040 (CH), 1720, 1665 (C=O), and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 260 nm (ϵ , 26,000) and 295 (3,000, sh).

^1H NMR spectrum (CDCl_3): δ 6.90-8.31 (m, aromatic).

Anal. Calcd for $\text{C}_{37}\text{H}_{24}\text{O}_4$: C, 83.46; H, 4.51. Found: C, 83.14; H, 4.32.

Methyl 8,9-Dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzo-cyclohepten-9-one-6-carboxylate (19c). 19c was obtained in a 86% yield, mp 183-184 °C.

IR spectrum ν_{\max} (KBr): 3040, 3020, 2940, 2900 (CH), 1718, 1710 (C=O), and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 252 nm (ϵ , 27,500) and 305 (5,200).

^1H NMR spectrum (CDCl_3): δ 3.49 (3 H, s, methoxy) and 6.80–7.71 (19 H, m, aromatic).

Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{O}_4$: C, 81.22; H, 4.80. Found: C, 81.49; H, 4.65.

8,9-Dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19d). 19d was obtained in a 82% yield, mp 220–221 °C.

IR spectrum ν_{max} (KBr): 3045, 3020, 2920 (CH), 1698 (C=O), and 1590 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 248 nm (ϵ , 49,000) and 290 (11,000).

^1H NMR spectrum (CDCl_3): δ 6.52–8.10 (m, aromatic and vinylic).

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_2$: C, 87.00; H, 5.00. Found: C, 86.83; H, 4.76.

Dimethyl 8,9-Dihydro-5-methyl-8-phenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (22). Preparation of 3-Methyl-2-phenyl-2,3-epoxyindanone (21). To a solution of 3-methyl-2-phenylindenone^{55,56} (2.2 g, 10 mmol) in methanol (150 mL) was added a solution of hydrogen peroxide (15%, 5 mL), containing sodium hydroxide (2 N, 5 mL). The mixture was stirred for 0.5 h and then diluted with water (50 mL). The solid that separated out, on cooling the mixture, was filtered and recrystallized from methanol to give 1.79 g (72%) of 21, mp 96–97 °C.

IR spectrum ν_{\max} (KBr): 3080, 3045, 3025, 2960, 2920 (CH), 1725 (C=O), and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 252 nm (ϵ , 28,000) and 296 (4,500).

^1H NMR spectrum (CDCl_3): δ 1.82 (3 H, s, methyl) and 7.34-7.96 (9 H, m, aromatic).

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_2$: C, 81.35; H, 5.08. Found: C, 81.13; H, 4.98.

A. Attempted Preparation of 22 Under Thermal Conditions.

A mixture of 21 (1.0 g, 4.2 mmol) and DMAD (18b, 600 mg, 4.2 mmol) in *o*-dichlorobenzene (10 mL) was refluxed for 15 min. Removal of the solvent and unreacted DMAD under vacuum gave a residue, which was recrystallized from a mixture (1:4) of benzene and petroleum ether to give 800 mg (80%) of 2-hydroxy-3-methylene-2-phenylindanone (20), mp 104-105 $^{\circ}\text{C}$.

IR spectrum ν_{\max} (KBr): 3400 (OH), 3080, 3065, 3020, 2920, 2840 (CH), 1710 (C=O), 1640 and 1595 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 235 nm (ϵ , 12,500), 253 (6,500), 260 (6,000), and 322 (800).

^1H NMR spectrum (CDCl_3): δ 3.23 (1 H, s, OH, D_2O -exchangeable), 5.50 (1 H, s, methylene), 5.95 (1 H, s, methylene), and 7.25-8.05 (9 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 236 (M^+ , 88), 235 ($\text{M}^+ - \text{H}$, 6), 208 ($\text{M}^+ - \text{CO}$, 7), 207 ($\text{M}^+ - \text{CO} - \text{H}$, 9),

158 ($M^+ - C_6H_5$, - H, 5), 131 ($M^+ - COC_6H_5$, 7), 105 ($C_6H_5CO^+$, 100), and other peaks.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.35; H, 5.08. Found: C, 81.13; H, 4.98.

In a separate experiment, 21 (500 mg, 2.1 mmol) in o-dichlorobenzene (5 mL) was refluxed for 10 min and removal of the solvent under vacuum gave 470 mg (94%) of 20, mp 104-105 °C (mixture mp).

B. Preparation of 22 Under Photochemical Conditions.

A mixture of 21 (1.09 g, 4.2 mmol) and DMAD (18b, 600 mg, 4.2 mmol) in acetone (600 mL) was irradiated (RPR, 2537 Å) for 30 min. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 150 mg (15%) of 4-methyl-3-phenylisocoumarin (23), mp 116-117 °C, after recrystallization from petroleum ether.

IR spectrum ν_{max} (KBr): 3060, 2995, 2910 (CH), 1718 (C=O), 1625 and 1595 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 230 nm (ϵ , 32,500), 282 (24,500), and 328 (9,000).

1H NMR spectrum ($CDCl_3$): δ 2.23 (3 H, s, methyl) and 7.15-8.30 (9 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 236 (M^+ , 100), 208 ($M^+ - CO$, 98), 207 ($M^+ - CO$, - H, 37), 131 ($M^+ - COC_6H_5$, 5), and other peaks.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.35; H, 5.08. Found: C, 81.21; H, 5.25.

Continued elution of the column with a mixture (1:1) of benzene and petroleum ether gave 20 mg (2%) of the dimer 24, mp 334–335 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3090, 3060, 3030, 2995, 2940 (CH), 1682 (C=O), and 1595 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 248 nm (ϵ , 68,700), 292 (9,400), and 302 (8,000).

^1H NMR spectrum (CDCl_3): δ 2.10 (6 H, s, methyl) and 6.16–8.27 (18 H, m, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 23.40 (CH_3), 78.48 ($\text{sp}^3\text{-C}$), 82.07 ($\text{sp}^3\text{-C}$), 126.13, 126.30, 126.99, 127.02, 127.06, 127.09, 127.13, 127.16, 127.23, 127.41, 127.60, 127.71, 127.82, 127.85, 127.88, 128.02, 128.19, 131.40, 132.44, 136.42, 142.61, and 194.36 (C=O).

Mass spectrum, m/e (relative intensity): 236 ($M^+/2$, 100), 219 ($M^+/2$, - OH, 2), 208 ($M^+/2$, - CO, 18), 207 ($M^+/2$, - CO, - H, 9), 159 ($M^+/2$, - C_6H_5 , 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 55), and other peaks.

Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.35; H, 5.08. Found: C, 81.25; H, 5.01.

Subsequent elution of the column with a mixture (9:1) of benzene and ethyl acetate gave the adduct 22 (1.0 g, 63%)

as a viscous liquid.

IR spectrum ν_{\max} (neat): 3080, 3060, 2940, 2845 (CH), 1725, 1710 (C=O), 1615 and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 240 nm (ϵ , 22,500), 243 (22,000), 246 (21,900), and 280 (12,300).

^1H NMR spectrum (CDCl_3): δ 1.79 (3 H, s, methyl), 3.70 (3 H, s, methoxy), 3.91 (3 H, s, methoxy), and 7.19–7.95 (9 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 378 (M^+ , 2), 377 ($\text{M}^+ - \text{H}$, 6), 348 ($\text{M}^+ - \text{CH}_2\text{O}$, 2), 347 ($\text{M}^+ - \text{OCH}_3$, 5), 319 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_6$: C, 69.84; H, 4.76. Found: C, 69.58; H, 4.85.

In a separate experiment, a solution of 21 (500 mg, 2.1 mmol) in acetone (250 mL) was irradiated (RPR, 2537 Å) for 30 min. Removal of the solvent under vacuum gave a residue, which on workup as in the earlier case gave 90 mg (18%) of 23, mp 116–117 °C (mixture mp) and 350 mg (70%) of the dimer 24, mp 334–335 °C (mixture mp). In yet another run, a solution of 21 (500 mg, 2.1 mmol) was irradiated in benzene (250 mL) for 30 min. Workup as in the earlier cases gave a mixture of the isocoumarin 23 (185 mg, 37%), mp 116–117 °C (mixture mp), the dimer 24 (150 mg, 30%), mp 334–335 °C (mixture mp), and some unchanged starting material (21) (95 mg, 19%), mp 96–97 °C (mixture mp).

I.4.3 Photolysis of 6,7-Dibenzoyl-8,9-dihydro-5,8,di-phenyl-5H-5,8-epoxybenzocyclohepten-9-one (19a). A solution of 19a (270 mg, 0.51 mmol) in acetone (300 mL) was irradiated for 1.5 h (RPR, 3000 Å). After removal of the solvent under vacuum, the residual solid was chromatographed over silica gel. Elution with a mixture (3:2) of benzene and petroleum ether gave 150 mg (55%) of the unchanged starting material 19a, mp 205-206 °C (mixture mp). Further elution with a mixture (9:1) of benzene and ethyl acetate gave 90 mg (33%) of 25a, mp 139-140 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3085, 3060, 3020 (CH), 1730, 1670, 1645 (C=O), 1625 and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 245 nm (ϵ , 47,000), 285 (16,000), and 312 (8,800, sh).

^1H NMR spectrum (CDCl_3): δ 6.80-8.20 (m, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 81.12 ($\text{sp}^3\text{-C}$), 96.48 ($\text{sp}^3\text{-C}$), 113.76, 124.31, 124.58, 126.48, 127.25, 127.88, 128.26, 128.40, 128.61, 128.97, 129.24, 129.29, 130.73, 130.92, 131.76, 131.86, 135.64, 136.15, 136.82, 137.32, 137.66, 152.51, 163.76, 190.51 (C=O), 195.14 (C=O), and 196.63 (C=O).

Mass spectrum, m/e (relative intensity): 532 (M^+ , 4), 427 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 2), 411 ($\text{M}^+ - \text{CO}_2$, - C_6H_5 , 3), 306 ($\text{M}^+ - \text{CO}_2$, - C_6H_5 , - COC_6H_5 , 11), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $C_{37}H_{24}O_4$: C, 83.46; H, 4.51. Found: C, 83.18; H, 4.52.

In another experiment, a solution of 19a (270 mg, 0.51 mmol) in benzene (300 mL) was irradiated for 2 h and worked up as in the previous case to give a mixture of 25a (50 mg, 19%) and the unchanged 19a (190 mg, 70%). In a repeat run, irradiation of 19a (270 mg, 0.51 mmol) in a mixture (1:9) of benzene and methanol (300 mL), under analogous conditions, gave a mixture of 25a (80 mg, 30%) and some unchanged 19a (162 mg, 60%).

Reaction of 25a with Sodium Methoxide. A mixture of 25a (100 mg, 0.19 mmol) and sodium methoxide (10 mg, 0.43 mmol) in methanol (10 mL) was stirred at room temperature ($\sim 25^\circ\text{C}$) for 12 h and later neutralized with hydrochloric acid (5%). Extraction with ether and removal of the solvent under vacuum gave a solid, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give the enol-ester 29a (75 mg, 70%), mp $175\text{--}176^\circ\text{C}$.

IR spectrum ν_{max} (KBr): 3420 (OH, intramolecularly hydrogen bonded), 3060, 2965, 2940 (CH), 1725, 1650, 1645 (C=O), and 1590 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 253 nm (ϵ , 24,000), 285 (14,000), and 365 (11,800).

^1H NMR spectrum (CDCl_3): δ 3.45 (3 H, s, methoxy), 6.67–8.10 (24 H, m, aromatic), and 17.35 (1 H, s, enolic OH, D_2O -exchangeable).

Mass spectrum, m/e (relative intensity): 564 (M^+ , 16), 533 ($M^+ - OCH_3$, 2), 505 ($M^+ - CO_2CH_3$, 1), 459 ($M^+ - COC_6H_5$, 3), 428 ($M^+ - OCH_3$, - COC_6H_5 , 3), 295 ($M^+ - CO_2CH_3$, - 2 COC_6H_5 , 2), 105 ($C_6H_5CO^+$, 100), and other peaks.

Anal. Calcd for $C_{38}H_{28}O_5$: C, 80.85; H, 4.96. Found: C, 80.57; H, 5.13.

Acetylation of 29a. A mixture of 29a (100 mg, 0.18 mmol), acetic anhydride (2 mL) and pyridine (2 mL) in dry benzene (10 mL) was stirred for 3 h at ca. 25 °C and poured on to crushed ice. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give a solid, which was recrystallized from a mixture (1:4) of benzene and petroleum ether to give 45 mg (42%) of 30a, mp 186-188 °C.

IR spectrum ν_{max} (KBr): 3060, 3025, 2980, 2925, 2820 (CH), 1765, 1730, 1665 (C=O), 1600 and 1585 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 238 nm (ϵ , 52,000), 253 (46,000), 262 (51,000), and 280 (48,000).

1H NMR spectrum ($CDCl_3$): δ 2.11 (3 H, s, methyl), 3.62 (3 H, s, methoxy), and 6.90-7.71 (24 H, m, aromatic).

Anal. Calcd for $C_{40}H_{30}O_6$: C, 79.20; H, 4.95. Found: C, 78.95; H, 4.67.

I.4.4 Photolysis of Dimethyl 8,9-Dihydro-5,8-diphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6,7-dicarboxylate (19b). A

solution of 19b (220 mg, 0.5 mmol) in acetone (200 mL) was irradiated (RPR, 2537 Å) for 2.5 h at ca. 25 °C. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (9:1) of benzene and ethyl acetate gave 155 mg (70%) of 25b, mp 178–179 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3040, 3015, 2980, 2995 (CH), 1732, 1715, 1700 (C=O), 1625 and 1585 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 240 nm (ϵ , 32,000), 280 (16,500), and 285 (16,000).

^1H NMR spectrum (CDCl_3): δ 3.18 (3 H, s, methoxy), 3.75 (3 H, s, methoxy), and 7.15–8.10 (14 H, m, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 51.32 (OCH_3); 51.95 (OCH_3), 96.22 ($\text{sp}^3\text{-C}$), 103.16 ($\text{sp}^3\text{-C}$), 124.48, 126.49, 126.97, 127.18, 127.44, 127.66, 127.79, 128.19, 128.34, 128.54, 128.75, 128.82, 129.22, 129.45, 130.88, 131.08, 136.05, 136.13, 136.92, 151.37, 163.72, 166.96 (C=O), 167.86 (C=O), and 195.36 (C=O).

Mass spectrum, m/e (relative intensity): 440 (M^+ , 35), 409 ($\text{M}^+ - \text{OCH}_3$, 11), 381 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 10), 350 ($\text{M}^+ - \text{CO}_2\text{CH}_3 - \text{OCH}_3$, 4), 322 ($\text{M}^+ - 2 \text{CO}_2\text{CH}_3$, 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_6$: C, 73.63; H, 4.55. Found: C, 73.31; H, 4.56.

In a repeat run, a solution of 19b (220 mg, 0.5 mmol) was irradiated in benzene (200 mL), under analogous conditions, to give a 60% (132 mg) yield of 25b. Similarly, the irradiation of a solution of 19b (220 mg, 0.5 mmol) in a mixture (1:9) of benzene and methanol (200 mL) gave a 66% (145 mg) of 25b.

Reaction of 25b with Sodium Methoxide. A mixture of 25b (100 mg, 0.23 mmol) and sodium methoxide (25 mg, 0.46 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature ($\sim 25^\circ\text{C}$) for 1 h and later neutralized with hydrochloric acid (5%). Extraction with ether and removal of the solvent under vacuum gave 60 mg (56%) of the enol ester 29b, mp 160–162 $^\circ\text{C}$, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3415 (OH, intramolecularly hydrogen bonded), 3080, 3060, 3020, 2945, 2885 (CH), 1725, 1700, 1645 (C=O), 1595 and 1570 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 241 nm (ϵ , 16,500), 250 (14,200), 255 (12,000), and 310 (9,500).

^1H NMR spectrum (CDCl_3): δ 3.30 (3 H, s, methoxy), 3.62 (3 H, s, methoxy), 3.71 (3 H, s, methoxy), 6.75–7.82 (14 H, m, aromatic), and 12.90 (1 H, s, enolic OH, D_2O -exchangeable).

Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_7$: C, 71.18; H, 5.08. Found: C, 71.29; H, 4.82.

I.4.5 Photolysis of Methyl 8,9-Dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one-6-carboxylate (19c). A

solution of 19c (230 mg, 0.5 mmol) in acetone (200 mL) was irradiated for 3.5 h (RPR, 2537 Å). Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with benzene gave 185 mg (80%) of 25c, mp 174-176 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3040, 3020, 2940, 2910 (CH), 1720, 1700 (C=O), and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 242 nm (ϵ , 58,000), 275 (31,000), and 320 (5,700, sh).

^1H NMR spectrum (CDCl_3): δ 3.10 (3 H, s, methoxy) and 7.15-7.95 (19 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 458 (M^+ , 4), 457 ($\text{M}^+ - \text{H}$, 10), 399 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, 1), 322 ($\text{M}^+ - \text{CO}_2\text{CH}_3$, - C_6H_5 , 5), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{O}_4$: C, 81.22; H, 4.80. Found: C, 80.91; H, 4.63.

In another experiment, a solution of 19c (230 mg, 0.5 mmol) in benzene (200 mL) was irradiated for 4 h and worked up as in the previous case to give a 62% (142 mg) of 25c, along with some (34 mg, 15%) unchanged starting material (19c). In another run, irradiation of a solution of 19c (230 mg, 0.5 mmol) in a mixture (1:9) of benzene and methanol (200 mL), under analogous conditions, gave a 55% (126 mg)

yield of 25c, along with a 18% (40 mg) of the unchanged starting material (19c).

I.4.6 Photolysis of 8,9-Dihydro-5,7,8-triphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19d). A solution of 19d (1.0 g, 2.5 mmol) in benzene (1 L) was irradiated for 3 h (RPR, 3000 Å). The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 300 mg (30%) of the unchanged 19d, mp 220-222 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 160 mg (16%) of 27d, mp 118-120 °C, after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether.

IR spectrum ν_{\max} (KBr): 3600 (OH), 3400 (OH, hydrogen bonded), 3060, 2920 (CH), 1648 (C=O), 1590 and 1580 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 245 nm (ϵ , 65,000) and 325 (7,500).

^1H NMR spectrum (CDCl_3): δ 5.75 (1 H, s, OH, D_2O -exchangeable) and 6.72-7.52 (19 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 400 (M^+ , 100), 327 ($\text{M}^+ - \text{C}_6\text{H}_5$, 85), 295 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 1), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 65), and other peaks.

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_2$: C, 87.00; H, 5.00. Found: C, 86.79; H, 4.75.

Further elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 430 mg (43%) of 25d, mp 192-193 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3020, 2920 (CH), 1718 (C=O), 1665 and 1600 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 250 nm (ϵ , 29,000) and 315 (3,000).

^1H NMR spectrum (CDCl_3): δ 6.80-7.75 (m, aromatic).

Mass spectrum, m/e (relative intensity): 400 (M^+ , 9), 323 ($\text{M}^+ - \text{C}_6\text{H}_5$, 2), 295 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 3), 267 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{CO}_2$, 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_2$: C, 87.00; H, 5.00. Found: C, 86.91; H, 4.93.

In a repeat run, a solution of 19d (400 mg, 1.0 mmol) in acetone (300 mL) was irradiated, under analogous conditions, for 3 h. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 27d (320 mg, 80%), mp 118-120 °C (mixture mp). Further elution with a mixture (9:1) of benzene and ethyl acetate gave 25d (20 mg, 5%), mp 192-193 °C (mixture mp).

In a repeat experiment, a solution of 19d (400 mg, 1.0 mmol) in benzene (300 mL), saturated with oxygen was

irradiated, under analogous conditions and worked up in the usual manner to give a mixture of 25d (132 mg, 33%) and some unchanged starting material (19d) (220 mg, 55%). In another experiment, a solution of 19d (400 mg, 1.0 mmol) in a mixture (1:9) of benzene and methanol (300 mL) was irradiated for 3 h and worked up as in the earlier cases to give a mixture of 25d (144 mg, 36%), 27d (52 mg, 13%), and unchanged starting material (19d) (88 mg, 22%).

I.4.7 Photolysis of 8,9-Dihydro-5,6,7,8-tetraphenyl-5H-5,8-epoxybenzocyclohepten-9-one (19e). A solution of 19e (250 mg, 0.53 mmol) in acetone (300 mL) was irradiated for 2.5 h (RPR, 3000 Å). The irradiation was repeated four times to photolyse, in all, 1.0 g (2.1 mmol) of 19e. Removal of the solvent from the combined photolysates gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 150 mg (15%) of 2,3,4-triphenyl-1-naphthol (28e), mp 160-161 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether (lit.²⁹ mp 161-162 °C). Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 250 mg (25%) of 4-benzoyl-2,3,4-triphenyl-4H-1-naphthone (26e), mp 164-166 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3020 (CH), 1670, 1640 (C=O), 1595 and 1575 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 253 nm (ϵ , 31,500) and 309 (8,000).

^1H NMR spectrum (CDCl_3): δ 6.51-7.70 (m, aromatic).

Mass spectrum, m/e (relative intensity): 476 (M^+ , 10), 371 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 4), 343 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{CO}$, 2), 294 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{C}_6\text{H}_5$, 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{35}\text{H}_{24}\text{O}_2$: C, 88.23; H, 5.04. Found: C, 87.96; H, 5.32.

Further elution with a mixture (9:1) of benzene and ethyl acetate gave 350 mg (35%) of the tricyclic compound 25e, mp 210-212 $^\circ\text{C}$, after recrystallization from a mixture (3:7) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3020, 2980 (CH), 1720 (C=O), 1670, 1600 and 1580 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 249 nm (ϵ , 31,000) and 300 (10,000).

^1H NMR spectrum (CDCl_3): δ 6.45-7.91 (m, aromatic).

Mass spectrum, m/e (relative intensity): 476 (M^+ , 13), 371 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 3), 294 ($\text{M}^+ - \text{COC}_6\text{H}_5 - \text{C}_6\text{H}_5$, 1), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{35}\text{H}_{24}\text{O}_2$: C, 88.23; H, 5.04. Found: C, 88.02; H, 5.31.

In a repeat experiment, a solution of 19e (476 mg, 1.0 mmol) in benzene (500 mL) was irradiated and worked up,

under analogous conditions, to give a mixture of 25e (142 mg, 30%), 26e (48 mg, 10%), 28e (26 mg, 7%), and the unchanged 19e (120 mg, 25%). In another experiment, irradiation of a solution of 19e (476 mg, 1.0 mmol) in a mixture (1:9) of benzene and methanol (500 mL), under analogous conditions, gave 157 mg (33%) of 25e, 24 mg (5%) of 26e, 93 mg (25%) of 28e, and 70 mg (15%) of the unchanged starting material, 19e.

Conversion of 26e to 28e. A mixture of 26e (50 mg, 0.11 mmol) and anhydrous aluminium chloride (50 mg, 0.37 mmol) in methylene chloride (15 mL) was stirred at ca. 25 °C for 5 h. The reaction mixture was treated with ice-cold water and extracted with ether. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give 25 mg (64%) of 27e, mp 160-161 °C (mixture mp).

I.4.8 Photolysis of Dimethyl 8,9-Dihydro-5-methyl-8-Phenyl-5H-5,8-epoxybenzocycloheptene-9-one-6,7-dicarboxylate (22). A solution of 22 (200 mg, 0.53 mmol) in acetone (200 mL) was irradiated (RPR, 2537 Å) for 8 h. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 50 mg (35%) of dimethyl 4-methyl-1-naphthol-2,3-dicarboxylate (32), mp 119-120 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether (lit.^{30,31} mp 119-120 °C). Further elution with a

mixture (9:1) of benzene and ethyl acetate gave 120 mg (60%) of the unchanged starting material, 22.

In a separate experiment, a solution of 22 (200 mg, 0.53 mmol) was irradiated in benzene (200 mL) under analogous conditions. Workup of the reaction mixture as in the earlier case gave 20 mg (14%) of 32, along with some unchanged starting material (22) (164 mg, 82%). In another run, irradiation of a solution of 22 (200 mg, 0.53 mmol) in methanol (200 mL) and workup as in the earlier cases gave 25 mg (17%) of 32, along with 130 mg (65%) of the unchanged 22.

Conversion of 32 to 36. A mixture of 32 (274 mg, 1 mmol) and concentrated hydrochloric acid (20 mL) was refluxed for 10 h. The reaction mixture was cooled and kept in a refrigerator for 12 h to give a solid, which was recrystallized from acetic acid to give 95 mg (47%) of 4-hydroxy-1-methyl-2-naphthoic acid (35), mp 205-207 °C (lit.³⁰ mp 202-207 °C).

A solution of 35 (92 mg, 0.4 mmol) in ether (10 mL) was treated with a freshly prepared solution of diazomethane in ether (~6% solution, 5 mL) at ca. 0 °C. The reaction mixture was stirred at ca. 0-5 °C for 35 h. Removal of the solvent under vacuum gave a residue, which was recrystallized from methanol to give 66 mg (63%) of methyl 4-methoxy-1-methylnaphthalene-2-carboxylate (36), mp 98-99 °C (lit.³⁰ mp 97-98 °C).

I.4.9 Thermolysis of 19a. A sample of 19a (2.0 g, 3.8 mmol) was heated at ca. 300-310 °C for 3 h in a sealed tube.

The thermolysate, after cooling, was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 640 mg (32%) of the unchanged starting material 19a, mp 205-206 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 75 mg (4%) of 39a, mp 184-185 °C, after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether (lit.⁵⁷ mp 185-187 °C). Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 500 mg (25%) of 25a, mp 139-140 °C (mixture mp).

In a separate experiment, a solution of 19a (150 mg, 0.28 mmol) in diphenyl ether (10 mL) was refluxed for 10 h. Workup of the reaction mixture in the usual manner gave 140 mg (93%) of the unchanged starting material 19a, mp 205-206 °C (mixture mp).

I.4.10 Thermolysis of 19b. A sample of 19b (2.0 g, 4.5 mmol) was heated at ca. 290-295 °C for 1.5 h in a sealed tube and the reaction mixture was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 38 mg (2%) of 1b, mp 158-160 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether (lit.⁷ mp 158-160 °C). Further elution with a mixture (3:7) of benzene and petroleum ether gave 55 mg (3%) of 39a, mp 228-229 °C, after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether (lit.⁵⁸ mp 228-229 °C).

Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 1.04 g (52%) of the unchanged 19b, mp 169-170 °C (mixture mp). Continued elution with a mixture (9:1) of benzene and ethyl acetate gave 140 mg (7%) of 25b, mp 178-179 °C (mixture mp).

In a repeat experiment, 19b (2.0 g, 4.5 mmol) was heated at ca. 290-300 °C for 3 h in a sealed tube and worked up as in the earlier case to give 630 mg (35%) of 39b and 400 mg (20%) of 25b.

In an attempted thermolysis, a solution of 19b (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h. Removal of the solvent under reduced pressure and crystallization of the residue from a mixture (1:9) of benzene and petroleum ether gave 145 mg (96%) of the unchanged 19b.

Transformation of 1b to 39b. A sample of 1b (150 mg, 0.36 mmol) was heated in a sealed tube at ca. 290-295 °C for 2 h. The thermolysate was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 80 mg (56%) of 39b, mp 228-229 °C (mixture mp).

I.4.11 Attempted Thermolysis of 25a. A solution of 25a (100 mg, 0.19 mmol) in diphenyl ether (10 mL) was refluxed for 20 h and worked up in the usual manner to give 90 mg (90%) of the unchanged starting material, 25a, mp 139-140 °C (mixture mp).

In a repeat experiment, 25a (0.5 g, 0.94 mmol) was heated

at ca. 300-310 °C for 1.5 h and worked up in the usual manner to give 150 mg (30%) of the unchanged starting material, 25a, mp 139-140 °C (mixture mp).

I.4.12 Attempted Thermolysis of 25b. A solution of 25b (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h and worked up in the usual manner to give 140 mg (93%) of the unchanged 25b, mp 178-179 °C (mixture mp).

In a repeat experiment, 25b (440 mg, 1.0 mmol) was heated in a sealed tube at ca. 295-300 °C for 1 h and worked up by chromatographing over silica gel. Elution with a mixture (9:1) of benzene and ethyl acetate gave 200 mg (45%) of the unchanged 25b, mp 178-179 °C (mixture mp).

I.4.13 X-Ray Crystallographic Analysis of 25a.⁵⁹ Suitable crystals (0.77 x 0.43 x 0.33) of 25a ($C_{37}H_{24}O_4$) for X-ray diffraction studies were obtained by recrystallization from a mixture (1:9) of benzene and petroleum ether. Data collections were performed with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD₄ computer-controlled kappa axis diffractometer equipped with graphite crystal, incident beam monochromator. The crystals have cell constants of $a = 10.884 (3) \text{ \AA}$, $b = 19.684 (5) \text{ \AA}$, $c = 17.129 (5) \text{ \AA}$, $\beta = 106.79 (3)^\circ$ and $V = 3513.1 (34) \text{ \AA}^3$. For $Z = 4$ and F. W. = 649.78 ($C_{46}H_{33}O_4$), the calculated density is 1.23 g/cm^3 and the observed density was $1.18 (2) \text{ g/cm}^3$. The space group was determined to be

$P2_1/n$. A total of 8001 reflections were collected, of which 6448 were unique and not systematically absent. Lorentz and polarization corrections were applied to the data. No absorption correction was made. All calculations were performed on a VAX 11/730 computer using the SDP/VAX⁶⁰ library and the DIRDIF program.

The structure was solved by direct methods using all of the observed data. The crystal structure consists of discrete molecular units at general positions. There are four molecules of the compound at general positions in the unit cell. In addition, there are six solvent molecules of benzene also in the unit cell. The phenyl ring portions of the compound are quite planar. The fused five membered rings are puckered with torsion angles ranging from 0.79 to 18.17°. The angle between the least-squares planes of the two five-membered rings is 71.53°.

I.4.14 Laser Flash Photolysis.³⁸ For laser flash photolysis, use was made of pulsed outputs from a UV-400 Molelectron nitrogen laser (337.1 nm, 2-3 mJ, ~8 ns) or a Quanta-Ray DCR-1 Nd-YAG laser (third harmonic, 355 nm, ~6 ns). The laser intensities were attenuated and kept in the range 2-10 mJ/pulse. The details of the kinetic spectrophotometer and data collecting system are described elsewhere.^{61,62} For transient spectra, a flow cell was used. For kinetics, static cells

(path lengths 1-3 mm) containing 1-2 mL of the solutions for photolysis were used. Unless the effect of oxygen was meant to be studied, the solutions were deaerated by saturating with high-purity argon.

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- (39) Occasionally, we have observed a weakly absorbing transient ($\lambda_{\text{max}} = 490 \text{ nm}$, $\tau \sim 10 \text{ } \mu\text{s}$) to be produced upon 337.1 or 355 nm laser flash photolysis of 19a in benzene. The decay of this transient is enhanced in the presence of oxygen ($k_q = 1.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and ferrocene ($k_q = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). Since a species with similar transient-spectral behaviour was not observed under triplet sensitization by benzophenone, an assignment of the 490 nm species in terms of the triplet of 19a appears untenable. On the other hand, 337.1 nm laser flash photolysis of the tricyclic compound 25a in benzene results in strong absorption signals due to its triplet ($\lambda_{\text{max}} = 490 \text{ nm}$) with decay and quenching behaviours similar to those of the transient species seen in the direct excitation of 19a. It is likely that the triplet of the photoproduct 25a is formed as a result of its formation from 19a and its excitation in the same laser pulse.
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CHAPTER II

PHOTOTRANSFORMATIONS OF BENZOYLAZIRIDINES

II.1 ABSTRACT

The phototransformations of a few benzoylaziridines such as trans-1-cyclohexyl-2,3-dibenzoylaziridine (21a), cis-1-cyclohexyl-2,3-dibenzoylaziridine (21b), trans-1-benzyl-2,3-dibenzoylaziridine (22), trans-2-phenyl-3-benzoylaziridine (23), and trans-1,3-dibenzoyl-2-phenylaziridine (24) have been examined by steady-state photolysis and product analysis. Laser flash photolysis studies of 21a,b, 22, 23 and a few other related substrates such as trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1a), cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1b), trans-2-p-anisyl-1-cyclohexyl-3-benzoylaziridine (25), cis-1-cyclohexyl-2-p-tolyl-3-benzoylaziridine (26), and cis-1-cyclohexyl-2-phenyl-3-p-anisoylaziridine (27) have also been carried out to explore the mechanisms of the observed phototransformations.

Irradiation of the dibenzoylaziridines 21a,b in benzene gave (Z)-1-cyclohexylamino-1,2-dibenzoylethylene (31), as the only isolable product. Similarly, 22, when irradiated in benzene gave (Z)-1-benzylamino-1,2-dibenzoylethylene (38), along with products such as trans-dibenzoylethylene (36) and benzaldehyde (37). Irradiation of 23 in benzene, on the other hand, gave a mixture of products such as 37, the dihydropyrazine 44, benzamide (46), acetophenone (47), 2,5-dibenzoyl-3,6-diphenylpyrazine (48), and 2,5-diphenylpyrazine (49). Irradiation of

24 gave a mixture of 2,5-diphenyloxazole (17), benzamide (46), and benzoic acid (55). Under the conditions of workup, the unchanged 24 underwent debenzoylation to give the aziridine 23.

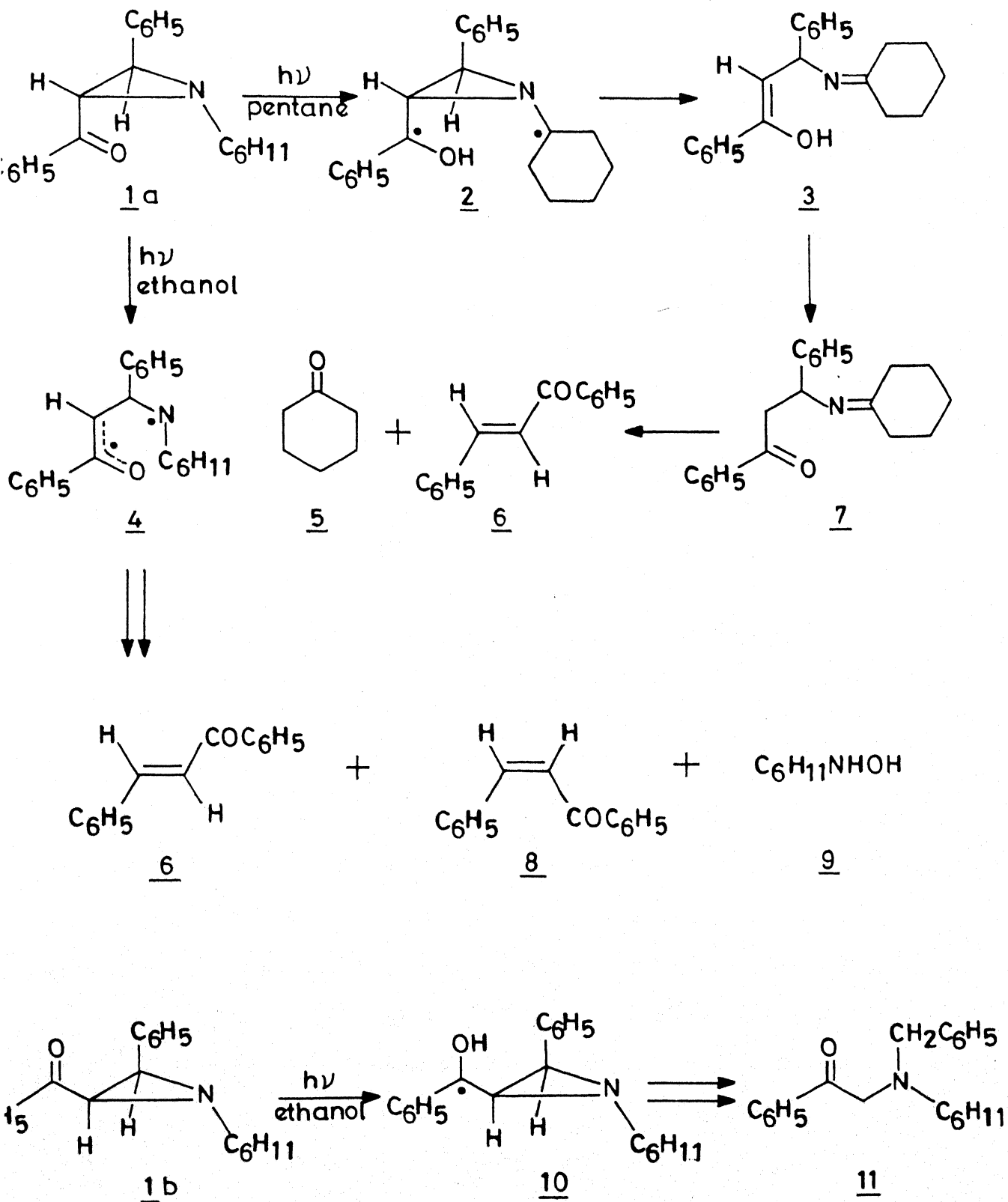
Nanosecond laser flash photolysis and pulse radiolysis of 2-aryl-3-benzoylaziridines and 2,3-dibenzoylaziridines in fluid solutions gave the corresponding azomethine ylides, characterized by absorptions at longer wavelengths (450-480 nm), and having lifetimes varying over a wide range ($\tau_Y = 1.5 \mu s - 300 ms$). The involvement of azomethine ylides was further confirmed by trapping them with dipolarophiles such as dimethyl acetylenedicarboxylate (DMAD). Thus, for example, irradiation of 1a in acetonitrile in the presence of DMAD gave a mixture of the pyrroline 57a and the pyrrole 58, whereas 1b, under analogous conditions gave the isomeric pyrroline 57b, along with the pyrrole 59b. Air and selenium dioxide oxidation of 57a and 57b, respectively gave the pyrrole 58. Irradiation of 21a in the presence of DMAD in acetonitrile gave the pyrroline 61, along with the pyrrole 63. Similar results were obtained when the irradiation of 21b was carried out in the presence of DMAD. Nickel peroxide oxidation of the pyrroline 61 in benzene gave the pyrrole 62. Short-lived triplets ($\leq 1 ns$) were involved as precursors for these ylides. Ketyl-type biradical intermediates formed via intramolecular electron or hydrogen atom transfer, were short lived, except in the case of 23. The laser excitation of 23 led to a permanent photoproduct, assigned as the 1,3-butadiene analogue 42, formed through the intermediacy of a relatively long-lived biradical 39.

II.2 INTRODUCTION

The photochemistry of arylaroylaziridines has attracted considerable attention due to their photochromic behaviour¹⁻⁵ and potential to undergo a variety of transformations. A few of the major reaction pathways followed by these systems include intramolecular hydrogen atom transfer, electrocyclic ring-opening to give azomethine ylides, and C-N bond cleavage leading to deamination.

Padwa and coworkers⁶⁻¹⁰ have investigated the photochemical transformations of several arylaroylaziridines and have shown that their photoreactions are strongly influenced by the nature of the substituents present in them and also the solvents employed. Thus, it has been observed that the irradiation of trans-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1a)⁸ in pentane, for example, gave a mixture of trans-benzalacetophenone (6) and cyclohexanone (5). The formation of 5 and 6 was explained in terms of an initial 1,5-hydrogen abstraction from the α -position of the N-substituent to give the biradical intermediate 2, followed by other transformations, as shown in Scheme II.1. The irradiation of 1a in ethanol, on the other hand, gave a mixture of trans-benzalacetophenone (6), cis-benzalacetophenone (8) and N-cyclohexylhydroxylamine (9). The initial reaction in this case has been assumed to be a C-N bond cleavage, giving rise to the biradical intermediate 4, which undergoes subsequent transformations to give the observed products (Scheme II.1). In contrast, the irradiation of the cis-

Scheme II.1

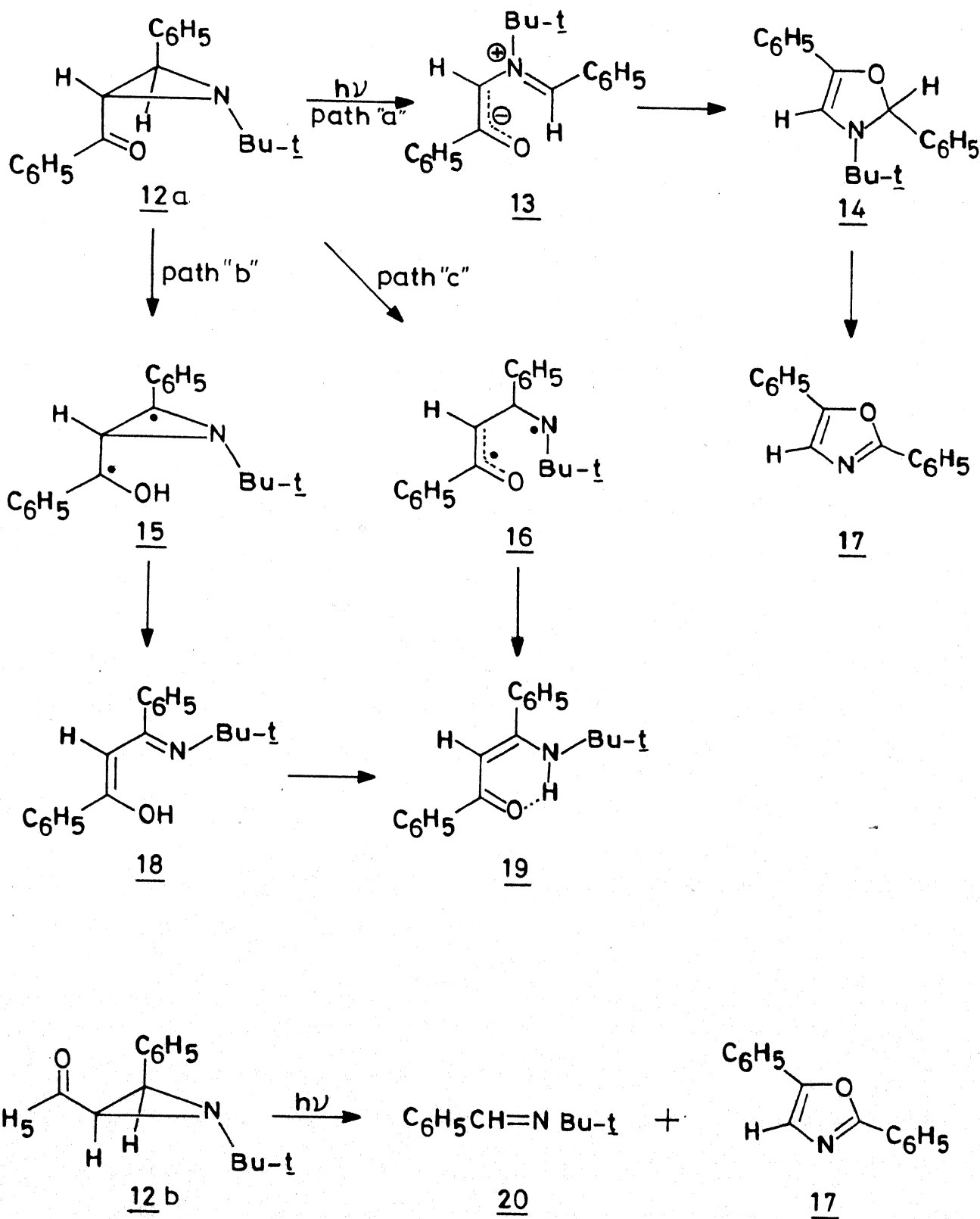


aziridine 1b in aqueous ethanol gave the phenacylamine derivative 11, arising through the intermediate 10. It may be mentioned in this connection that no products arising through azomethine ylide intermediates were formed in the irradiations of both 1a and 1b, under these conditions. However, it has been reported earlier that azomethine ylides are formed from arylaroylaziridines, when they are irradiated at 77 K in a suitable matrix.^{4,5} Earlier attempts to trap these azomethine ylides, by dimethyl acetylenedicarboxylate (DMAD) by irradiating a mixture of the starting aziridine with DMAD, were unsuccessful. However, mention may be made in this connection that Huisgen and coworkers¹¹⁻¹³ had successfully trapped the azomethine ylides, photogenerated from N-arylaziridine-2,3-dicarboxylates by DMAD in fluid solutions at room temperature.

In a later investigation, Padwa and coworkers^{8,10} have examined the photochemistry of a few arylaroylaziridines having no α -hydrogen on the N-substituent, such as trans-2-phenyl-3-benzoylaziridine (23) and the N-t-butyl substituted aziridines, 12a and 12b. Irradiation of 23 in protic solvents such as ethanol, for example, did not give any product. The trans-aziridine 12a, on the other hand, gave a mixture of 2,5-diphenyloxazole (17) and the ring-opened product, 19. The oxazole 17 in this reaction may be arising through the azomethine ylide 13, whereas the formation of 19 may be explained in terms of two distinct pathways, namely, 1,5-hydrogen atom transfer (path 'b') and C-N bond cleavage (path 'c'), as shown in

Scheme II.2. In contrast, irradiation of the cis-aziridine 12b gave a mixture of the oxazole 17 and fragmentation products such as 20, arising through hydrogen abstraction from the solvent (Scheme II.2). Based on these observations and deuterium labelling studies, path 'b', involving intramolecular hydrogen atom transfer has been implicated in the formation of 19.

Since intramolecular 1,5-hydrogen abstraction (either from the α -position of the N-substituent or the ring itself) is a major reaction pathway for the trans-arylaroylaziridines, we reasoned that the photoreactions of trans-2,3-diaroylaziridines should almost exclusively follow this pathway. Also, the photoreactions of cis-diaroylaziridines should not proceed through pathways involving initial hydrogen abstraction. In the present investigation, we have examined the photochemical transformations of a few 2,3-dibenzoylaziridines such as trans-1-cyclohexyl-2,3-dibenzoylaziridine (21a), cis-1-cyclohexyl-2,3-dibenzoylaziridine (21b), and trans-1-benzyl-2,3-dibenzoylaziridine (22), with a view to studying the nature of the products formed in these reactions and also their reaction pathways. Also, it was felt necessary to reinvestigate the photochemistry of trans-2-phenyl-3-benzoylaziridine (23), in the light of the reported phototransformations of 12a and 12b. In principle, 23 should undergo phototransformations involving 1,5-hydrogen atom transfer and electrocyclic ring-opening reactions (Scheme II.2). We have therefore, reexamined the photochemistry of 23 in a non-protic medium such as benzene. In addition, we have examined



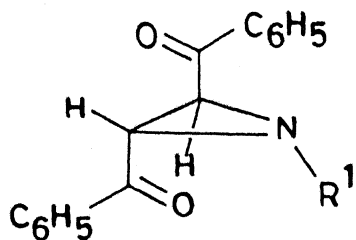
the photochemistry of trans-1,2-dibenzoyl-2-phenylaziridine (24), wherein, the electrocyclic ring-opening reaction is expected to be less favoured.

Laser flash photolysis studies involving both direct and sensitized excitation of 2la,b, 22, 23 and a few other arylaroylaziridines such as la,b, trans-2-p-anisyl-1-cyclohexyl-3-benzoylaziridine (25), cis-1-cyclohexyl-2-p-tolyl-3-benzoylaziridine (26) and cis-1-cyclohexyl-2-phenyl-3-p-anisoylaziridine (27) have also been carried out to gain information concerning the spin multiplicities of the excited states and also the involvement of biradical and azomethine ylide intermediates in these reactions. Attempts have also been made to trap the azomethine ylide intermediates through the irradiation of representative aziridines such as la,b and 2la,b in the presence of DMAD. Chart II.1 shows the structures of the different arylaroyl- and diaroylaziridines that we have employed in the present investigation.

II.3 RESULTS AND DISCUSSION

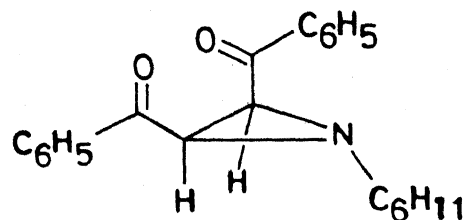
II.3.1 Preparative Photochemistry and Product Identification. Irradiation of a benzene solution of trans-1-cyclohexyl-2,3-dibenzoylaziridine (2la) for 4 h gave (Z)-1-cyclohexylamino-1,2-dibenzoylethylene (31) in a 52% yield, along with a 36% recovery of the unchanged 2la (Scheme II.3). Similarly, irradiation of the cis-aziridine 2lb, under analogous conditions, for 6.5 h gave a 32% yield of 31, along with the recovery of considerable amounts (54%) of the unchanged 2lb.

Chart II.1

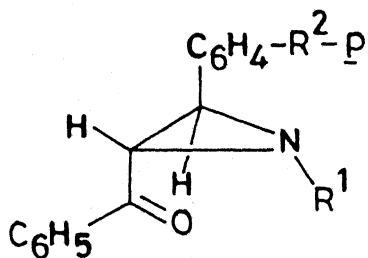


21 a) $R^1 = C_6H_{11}$

22) $R^1 = CH_2C_6H_5$



21 b

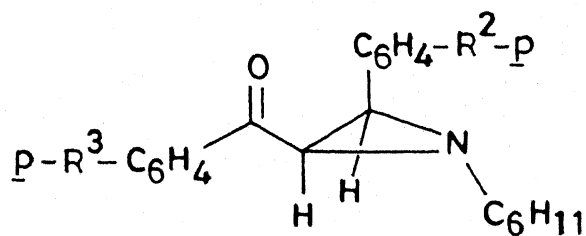


1 a) $R^1 = C_6H_{11}; R^2 = H$

23) $R^1 = R^2 = H$

24) $R^1 = COC_6H_5; R^2 = H$

25) $R^1 = C_6H_{11}; R^2 = OCH_3$

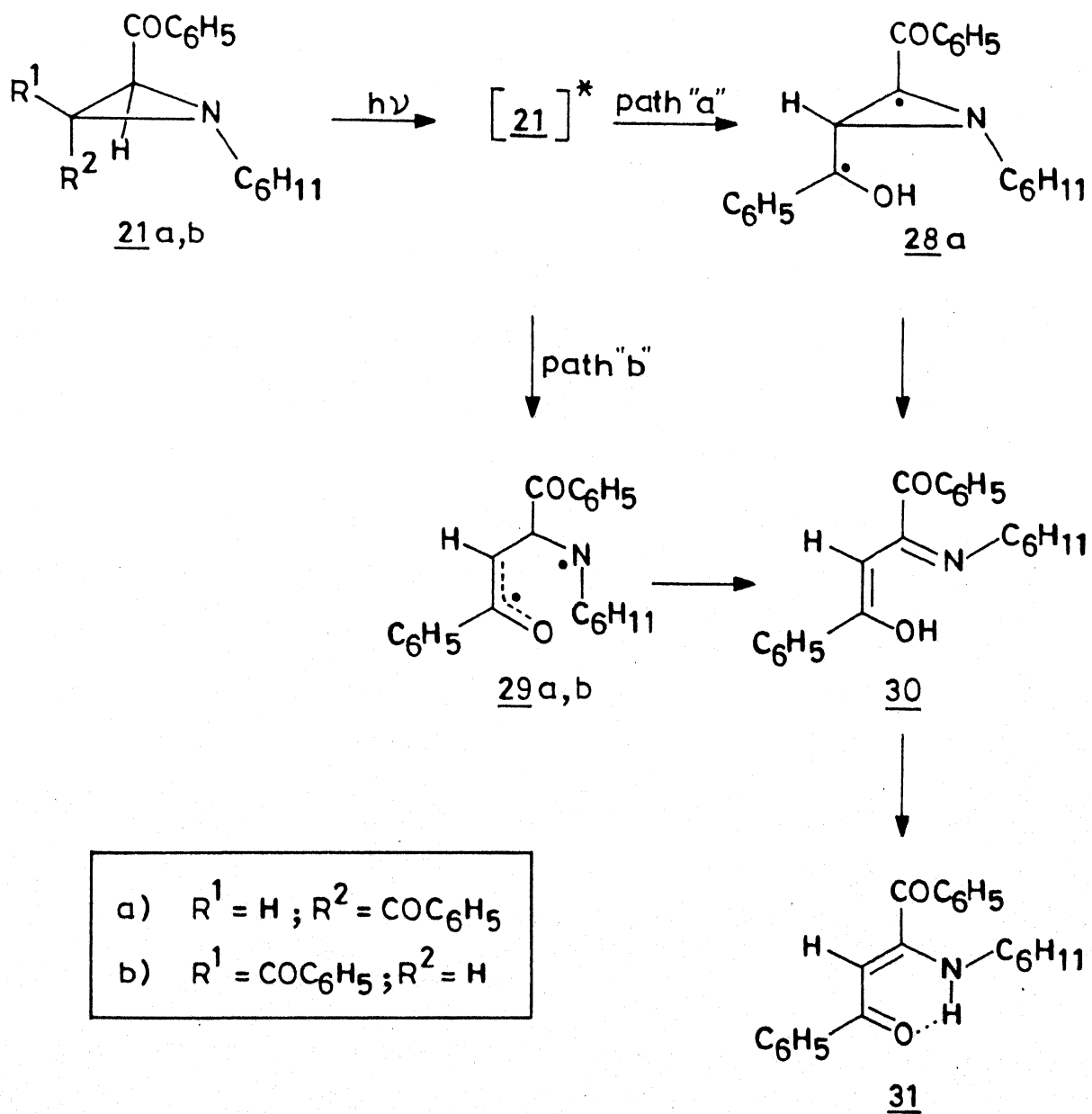


1 b) $R^2 = R^3 = H$

26) $R^2 = CH_3; R^3 = H$

27) $R^2 = H; R^3 = OCH_3$

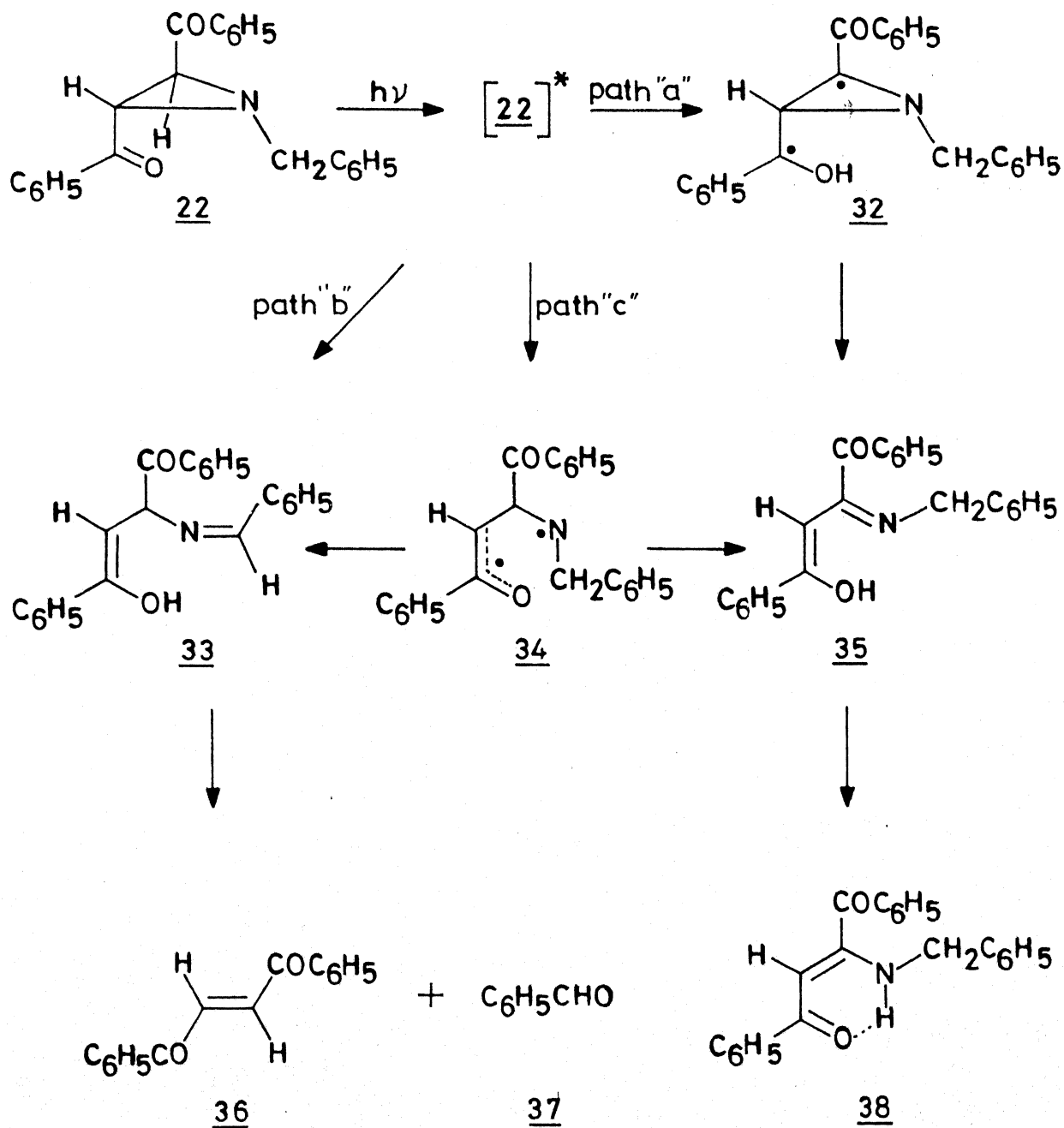
Scheme II.3



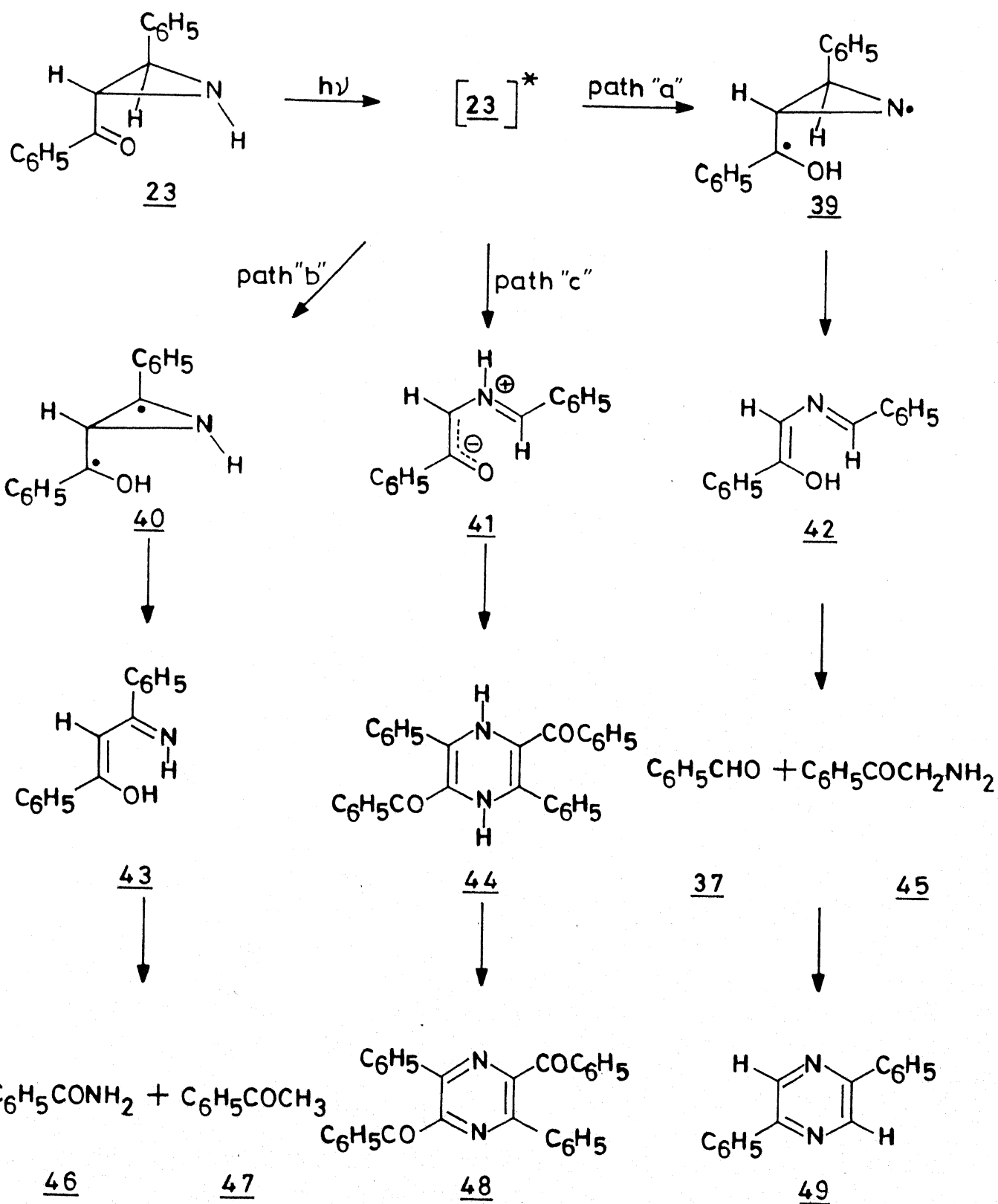
Irradiation of a benzene solution of trans-1-benzyl-2,3-di-benzoylaziridine (22) for 4 h, on the other hand, gave (Z)-1-benzylamino-1,2-dibenzoylethylene (38) in a 80% yield, along with small amounts of trans-dibenzoylethylene (36, 7%) and benzaldehyde (37, 6%) (Scheme II.4). In contrast to 21a,b and 22, irradiation of a benzene solution of trans-2-phenyl-3-benzoylaziridine (23) for 4.5 h gave several products such as benzaldehyde (37, 6%), the dihydropyrazine 44 (5%), benzamide (46, 4%), acetophenone (47, 3%), 2,5-dibenzoyl-3,6-diphenylpyrazine (48, 11%) and 2,5-diphenylpyrazine (49, 8%), along with a 32% recovery of the unchanged 23 (Scheme II.5). The structure of the pyrazine 48 was established on the basis of analytical results, spectral evidence and chemical transformations. Nickel peroxide oxidation of the dihydropyrazine 44 in benzene, for example, gave the pyrazine 48. In continuation, we have examined the photochemistry of 1,3-dibenzoyl-2-phenylaziridine (24), with a view to understanding the effect of an electron-withdrawing substituent at the 1-position in directing the reaction pathway. Irradiation of a benzene solution of 24 for 2 h gave a mixture of 2,5-diphenyloxazole (17, 12%), benzamide (46, 8%) and benzoic acid (55, 46%). Under the conditions of workup, the unchanged 24 underwent debenzoylation to give the aziridine 23 (52%) (Scheme II.6).

We have sought a convincing support for the generation of azomethine ylide intermediates in the photochemical ring-opening of aziridines, by carrying out the trapping studies on

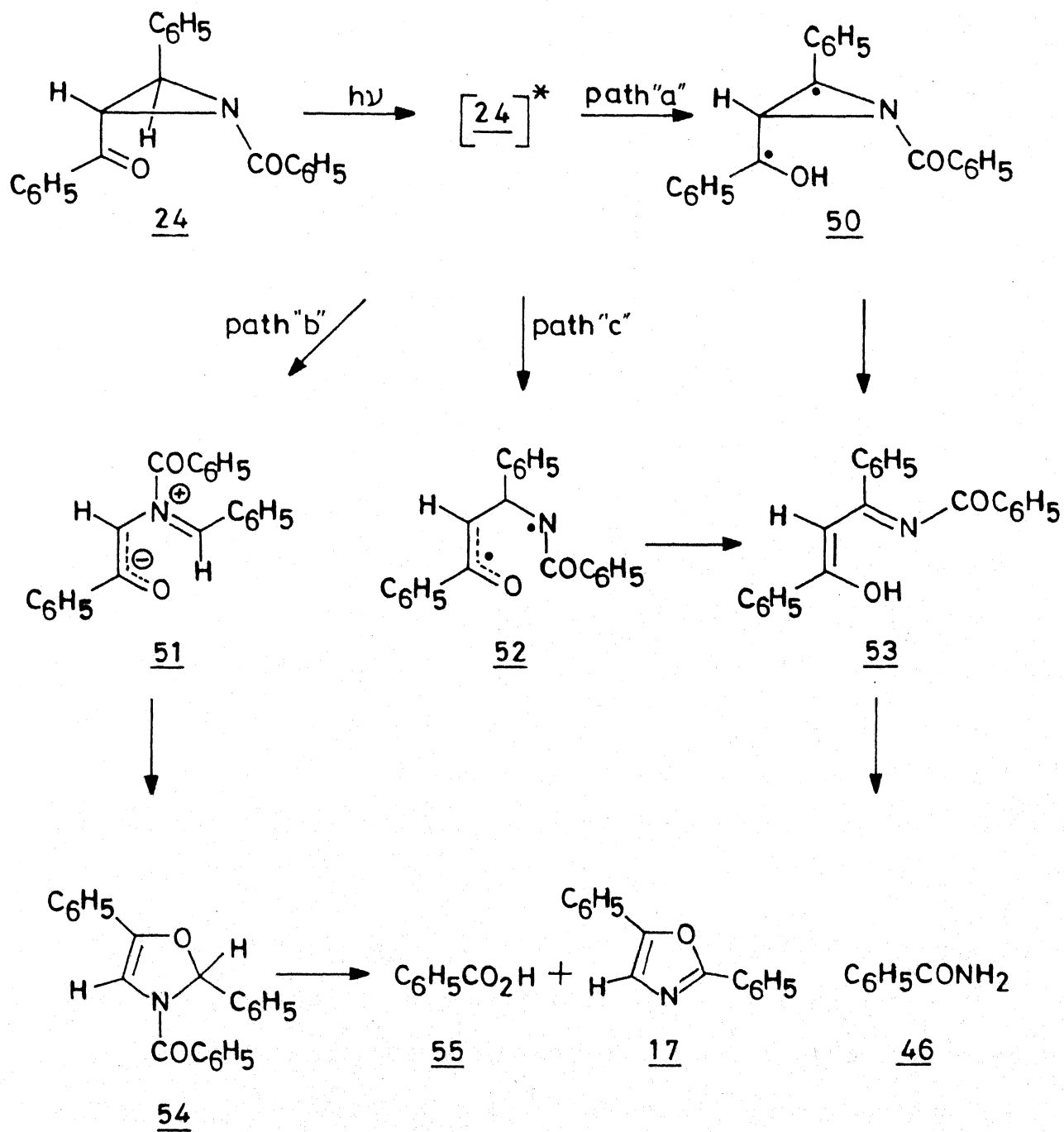
Scheme II.4



Scheme II.5

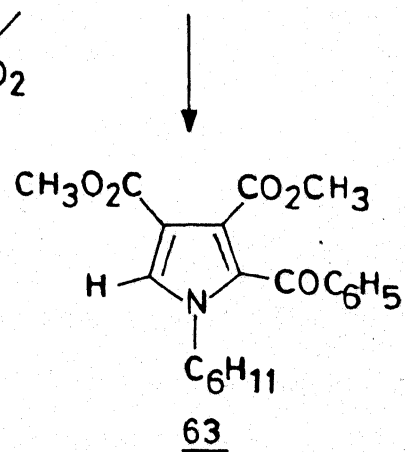
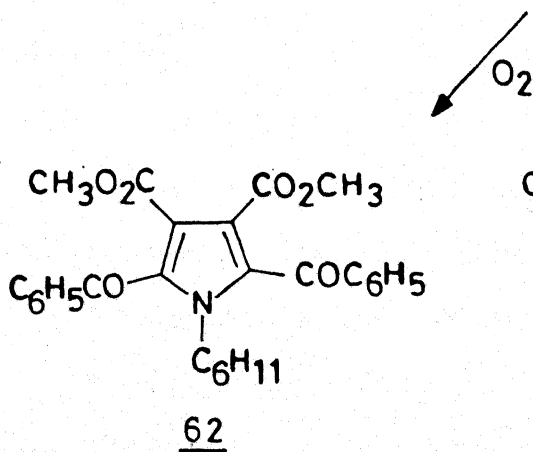
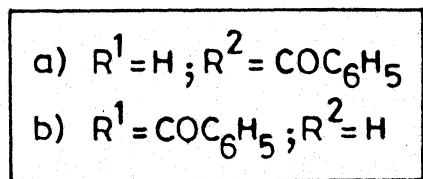
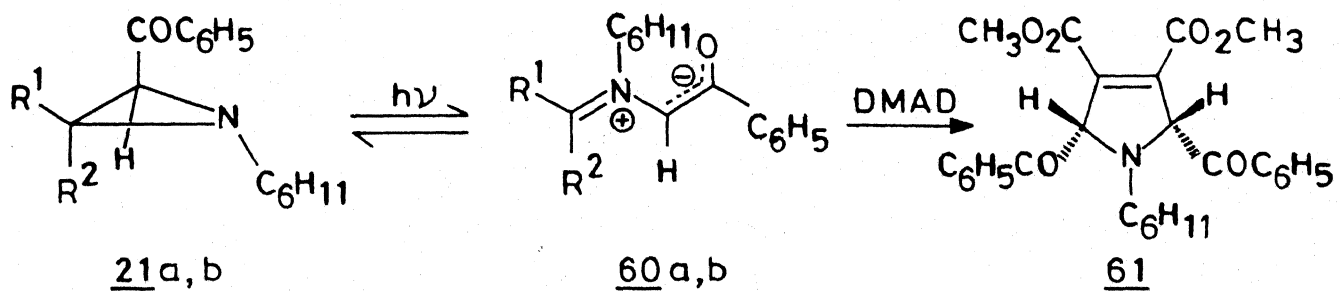
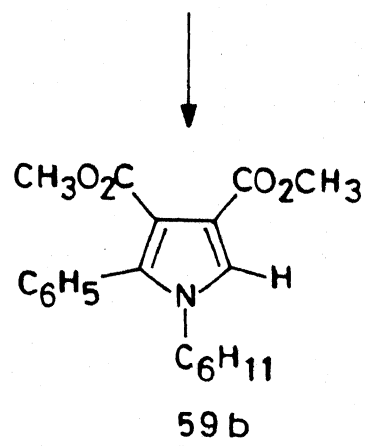
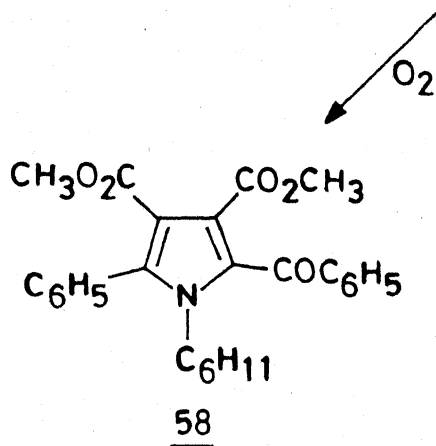
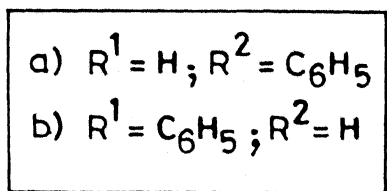
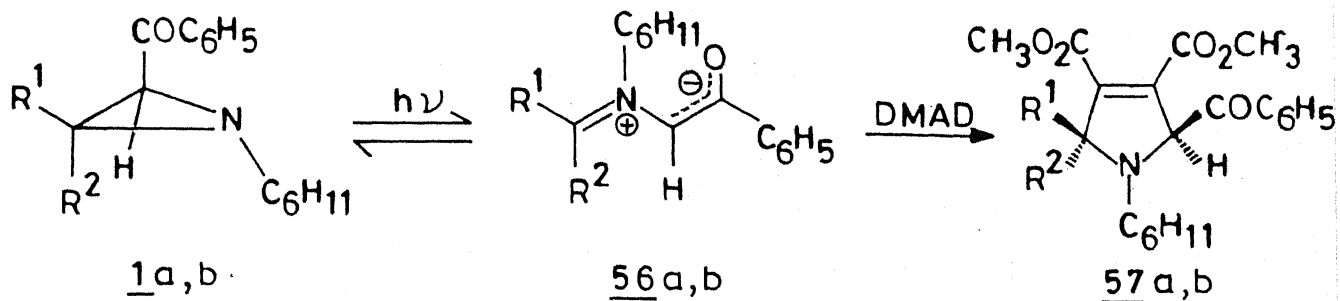


Scheme II.6



the cis-trans pairs 1a,b and 21a,b, as representative examples. Thus, for example, irradiation of 1a in the presence of DMAD, in acetonitrile, gave a mixture of the trans-3-pyrroline 57a (51%) and the pyrrole 58 (26%). Similarly, the irradiation of 1b in the presence of DMAD, under analogous conditions, gave a mixture of the cis-3-pyrroline 57b (62%), the pyrrole 59b (3%), and the unchanged 1b (20%) (Scheme II.7). The structures of the pyrrolines 57a,b were assigned on the basis of analytical results, spectral data and chemical evidence. Thus, for example, 57a, when refluxed in benzene under oxygen saturation gave the pyrrole 58, whereas the 57b underwent dehydrogenation to give the same pyrrole, 58, when treated with selenium dioxide. The stereochemistry of the pyrrolines 57a and 57b was assigned on the basis of their ^1H NMR spectra. The C-2 and C-5 protons in 57a, for example, appeared as two singlets at δ 3.32 and 3.63, respectively. The corresponding protons in 57b appeared at slightly upfield positions at δ 3.18 and 3.48, respectively. That the C-2 and C-5 protons in the cis-3-pyrrolines appear at upfield positions compared to the trans-isomers is reported in the literature for several pairs of cis- and trans-3-pyrrolines.^{11,14-19}

In contrast to 1a,b, the irradiation of both the trans-aziridine 21a and the cis-aziridine 21b in the presence of DMAD in acetonitrile gave similar mixtures of products consisting of the pyrrole 63 (2 and 3%) and the cis-3-pyrroline 61 (62 and 54%), along with small amounts of two unidentified



compounds. The structure of 61 was arrived at on the basis of analytical results, spectral data and chemical evidence. Thus, 61 on treatment with nickel peroxide in benzene gave the pyrrole 62. The stereochemistry of 61 is tentatively assigned as that of the cis-configuration. Our assignment is based on earlier reports,¹⁵⁻¹⁷ suggesting that the cis-3-pyrrolines are thermodynamically more stable than the corresponding trans-isomers due to the relief of nonbonded interactions between the N-alkyl group and the substituents at C-2 and C-5 positions.

II.3.2 Discussion. The formation of the various products in the phototransformations of aziridines 21a,b and 22-24 could be explained in terms of the pathways shown in Schemes II.3-II.6. Thus, the formation of the enaminedione 31 in the irradiation of 21a may be explained in terms of two distinct pathways (path 'a' and path 'b', Scheme II.3). Path 'a' involves a 1,5-hydrogen transfer from the excited state of 21a to give the biradical intermediate 28a, followed by further transformations. An alternative pathway (path 'b') involves the C-N bond cleavage, initiated by the carbonyl triplet to give the biradical 29a, and further transformations to give 31. Similar reaction pathways may be invoked for the formation of the enaminedione 38 from 22 (Scheme II.4). Earlier investigators¹⁰ had favoured a mechanism involving path 'a' in a similar transformation (see Scheme II.2). However, based on the following observation, we conclude that path 'b'

involving initial C-N bond cleavage is also partially contributing to product formation in the photolysis of 2,3-dibenzoylaziridines. If 1,5-hydrogen transfer (path 'a') is the only pathway followed, the cis-aziridine 21b, wherein this pathway is restricted, should not give a product such as 31. Contrary to this expectation, the irradiation of 21b also gave 31, albeit in a lower yield, compared to 21a. The formation of products such as trans-dibenzoylethylene (36) and benzaldehyde (37) in the irradiation of 22 may be explained through an intermediate such as 33, which in turn may be arising through the biradical 34, and/or through a 1,5-benzylic hydrogen transfer to the carbonyl oxygen, followed by C-N bond cleavage (for a similar transformation, see Scheme II.1).

Formation of the different products in the irradiation of 23 may be explained in terms of the pathways shown in Scheme II.5. On the basis of product analysis, three distinct reaction pathways may be envisaged. A 1,5-hydrogen abstraction (path 'a') in the excited state of 23 could give rise to the biradical intermediate 39, which can subsequently undergo ring-opening and other transformations to give phenacylamine (45) and benzaldehyde (37). The dimerization of 45,²⁰ under the conditions of workup will eventually lead to the pyrazine 49. A parallel reaction (path 'c') involves the azomethine ylide 41, which upon dimerization will give the dihydropyrazine 44. Further oxidation of 44, under the conditions of workup

can give rise to the pyrazine 48. Yet another mode of transformation of 23 involves a 1,5-hydrogen transfer (path 'b') from its excited state, leading to the biradical intermediate 40, which in turn, will lead to products such as benzamide (46) and acetophenone (47).

The phototransformations of 24, likewise, may be proceeding through different pathways. One of these involves the ring-opening of 24 to give the azomethine ylide 51, which in turn could undergo further transformation to give the oxazole 17 (path 'b', Scheme II.6). The formation of benzamide (46), on the other hand, could be explained on the basis of the intermediate 53, which in turn may arise through the biradical intermediate 50 (1,5-hydrogen transfer, path 'a') and/or through the biradical 52 (C-N bond cleavage, path 'c'), as shown in Scheme II.6.

II.3.3 Laser Flash Photolysis.^{21,22} In order to shed light on the intermediates participating in the photochemistry of aziridines, we have carried out nanosecond laser flash photolysis and pulse radiolysis of 1a,b, 21a,b, 22, 23 and 25-27. The transients were characterized on the basis of detailed sensitization and quenching studies and low-temperature photolysis, carried out in glass matrices.

a) Direct Laser Excitation. Laser flash photolysis (337.1 or 355 nm) of the 2-aryl-3-benzoylaziridines 1a,b and 25-27 in benzene at room temperature resulted in the formation of transient species (major), characterized by broad absorption

maxima (λ_{max}) at 470-475 nm and lifetimes (τ) in the range of 1.5-3.5 μs (Figures II.1 and II.2). The yield and decay kinetics of the major transients remained unchanged in the presence of oxygen (~ 2 mM). On going from benzene to methanol the lifetimes of the major transients become substantially longer (50-170 μs) and the absorption maxima become blue-shifted by 15-20 nm. The low temperature photolysis of 1a,b and 25-27 in glass matrices also gave species having similar spectral and kinetic characteristics. Following the decay of the major transients, residual absorptions (minor) were observed with lifetimes > 10 μs and absorption maxima at 440-450 nm. Concomitant with the decay at 470-475 nm, growths of absorptions due to photoproducts could be observed at 300-350 nm, which did not show any decay over ~ 150 μs (longest time domain available in the nanosecond laser flash photolysis setup). Similar spectral changes were observed upon prolonged irradiation of 1a in benzene (Figure II.1, parts C and C').

Laser excitation of 2,3-dibenzoylaziridines 21a,b and 22 in benzene gave a long-lived transient ($\lambda_{\text{max}} \sim 480$ nm), which undergo only 15-30% decay over 150 μs . The transient spectra in these cases were broad and structureless (Figure II.3, parts A-C). At 360-400 nm, additional minor absorptions with slightly shorter lifetimes were observed. The transient spectrum was insensitive to oxygen. In methanol, the major absorption maxima remained practically unchanged (relative to benzene); however slow growth components were noted over

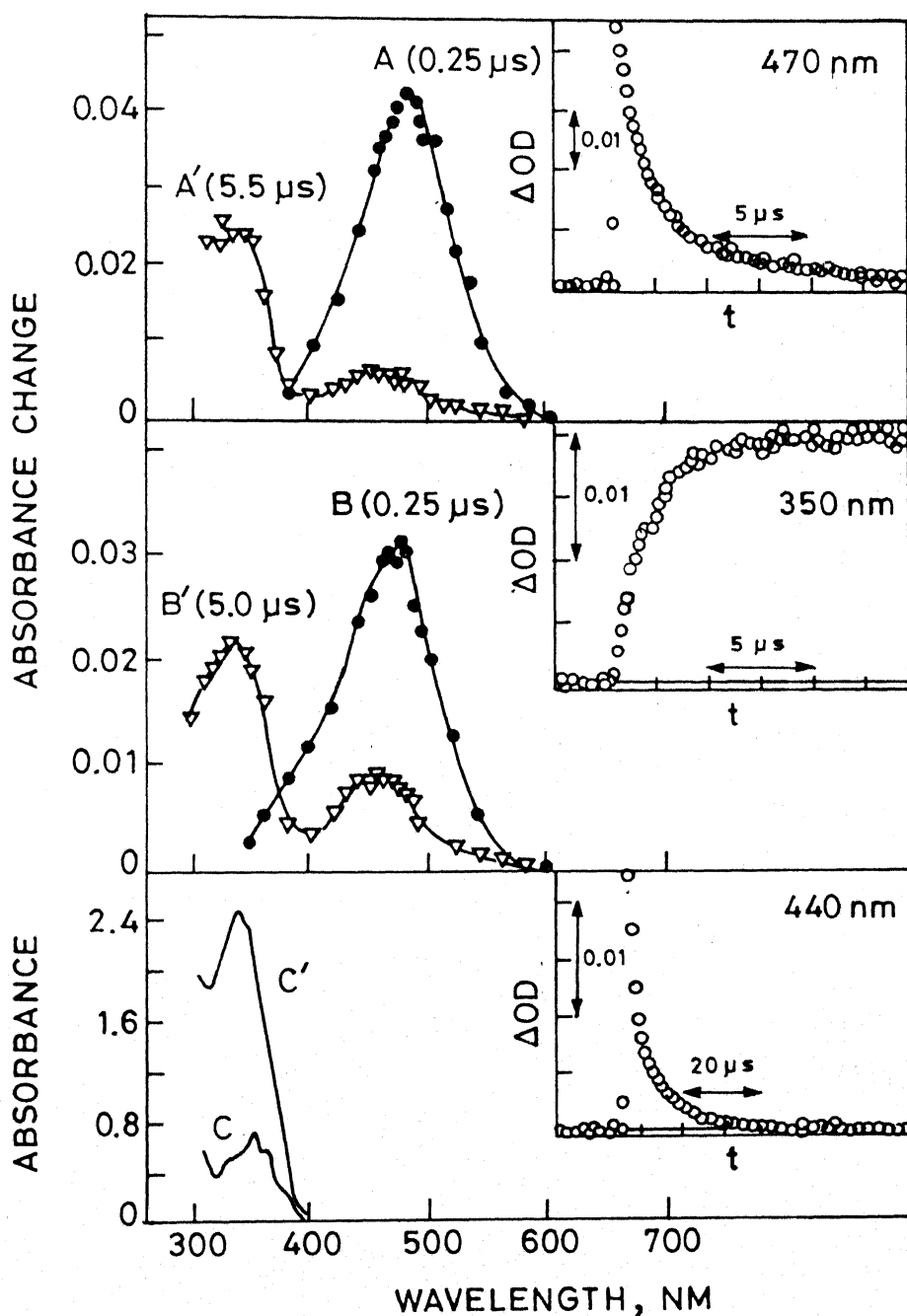


Fig. II.1 Transient absorption spectra following 337.1 nm laser excitation of (A, A') 1a and (B, B') 1b in benzene. The curves C and C' are the ground-state absorption spectra of 1a in benzene and of the photoproducts accumulated after prolonged exposure to 337.1 nm laser pulses. Insets: kinetic traces at the wavelengths indicated for 1a in benzene.

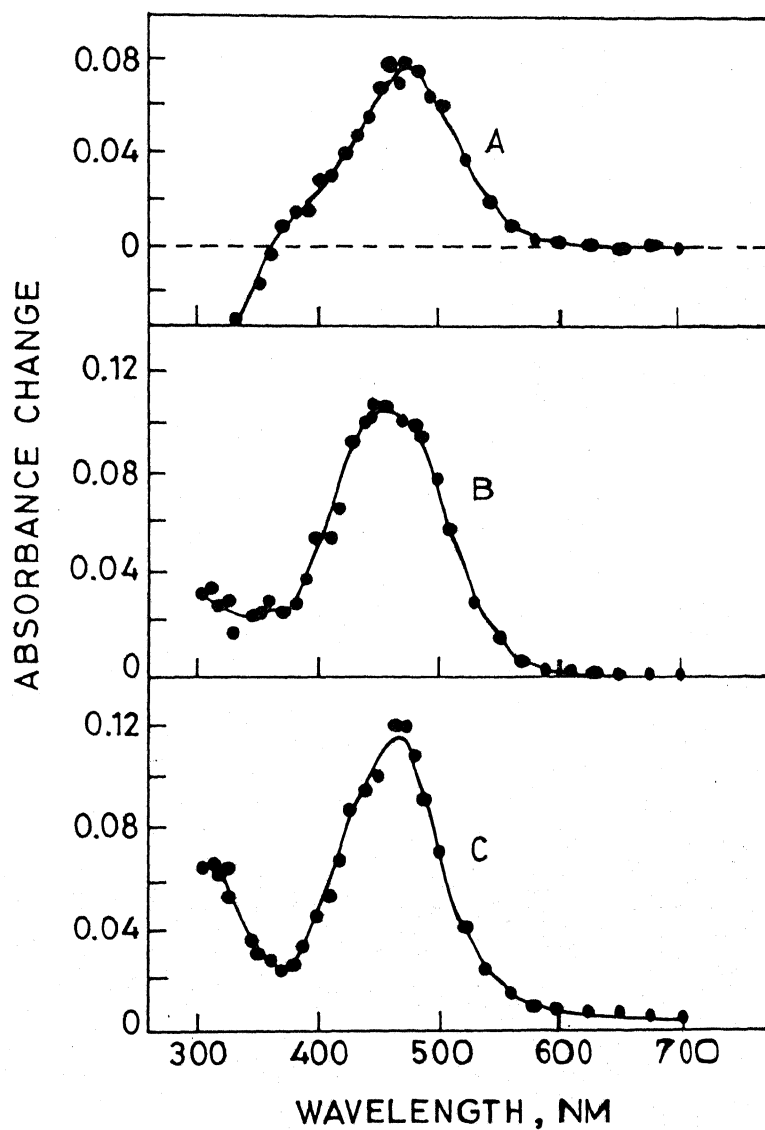
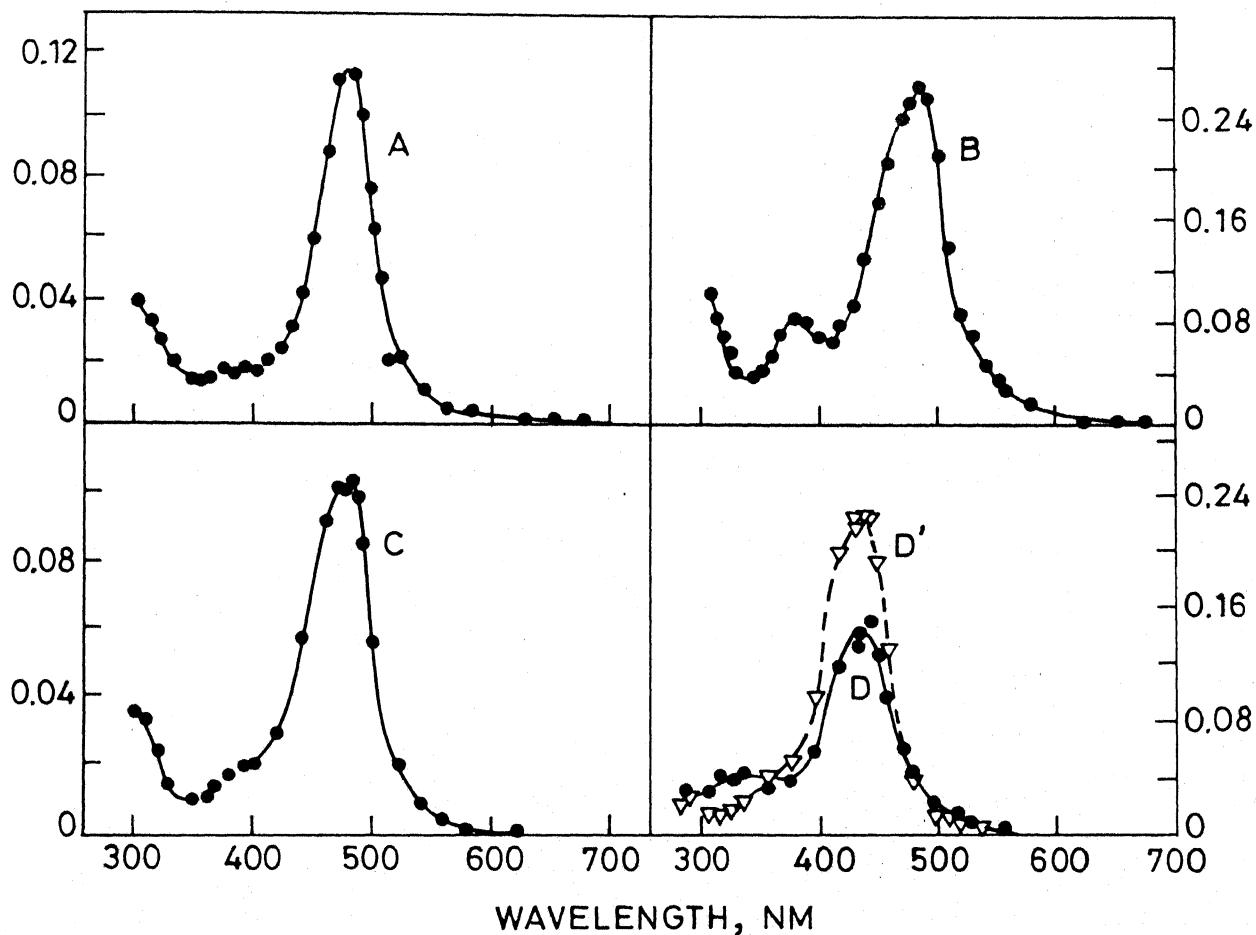


Fig. II.2 Transient absorption spectra observed in benzene solutions of (A) 25, (B) 26 and (C) 27 at 0.3, 0.3 and 0.2 μ s, respectively, following 337.1 nm laser excitation.



g. II.3 Transient absorption spectra observed upon 337.1nm laser excitation of (A) 21a in benzene, (B) 21b in benzene, (C) 22 in benzene and (D, D') 21b in methanol. The spectra correspond to (A) 1.0, (B) 1.0, (C) 0.5, (D) 1.0 and (D') 70 μ s, following the laser pulse.

100-150 μ s at wavelengths close to the major transients' maxima (Figure II.3, part D).

Laser-induced transient phenomena observed with 2-phenyl-3-benzoylaziridine (23) were quite different from 1a,b and 25-27. The laser excitation of 23 in benzene or methanol gave intense absorption changes due to a 'permanent' photoproduct ($\lambda_{\text{max}} = 360$ nm, Figure II.4) showing no sign of decay over ~ 150 μ s. In addition, there was indication of a minor long-lived transient ($\tau > 150$ μ s) appearing as a shoulder at 400-500 nm. Prolonged irradiation of 23 with repetitive 337.1 nm laser pulses gave a permanent photoproduct, with absorption spectrum superimposable on that of the major product seen in the time-resolved experiment. On a short time scale (1-2 μ s) following the laser pulse, transient processes were observed in the form of a fast growth component for the 360 nm species and the concomitant decay of the transient absorption ($\tau = 110 \pm 10$ ns) at 450-500 nm. The kinetics of these processes were enhanced in the presence of oxygen ($k_{q,O_2} = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ in benzene) but were not affected by 2,5-dimethyl-2,4-hexadiene (DMHD, 35 mM), 1-methylnaphthalene (MN, 30 mM), and ferrocene (10 mM), suggesting that the fast component to be a biradical.

For each of the substrates in benzene and methanol, estimates were made for products of photoproduct yield (Φ_P) and extinction coefficient (ϵ_{max}^P) by comparing the absorbance change at the respective wavelength maximum with that due to the benzophenone triplet ($\Phi_T = 1$, $\lambda_{\text{max}}^T = 532$ nm, $\epsilon_{\text{max}}^T = 7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)²³ in an optically matched benzene solution.

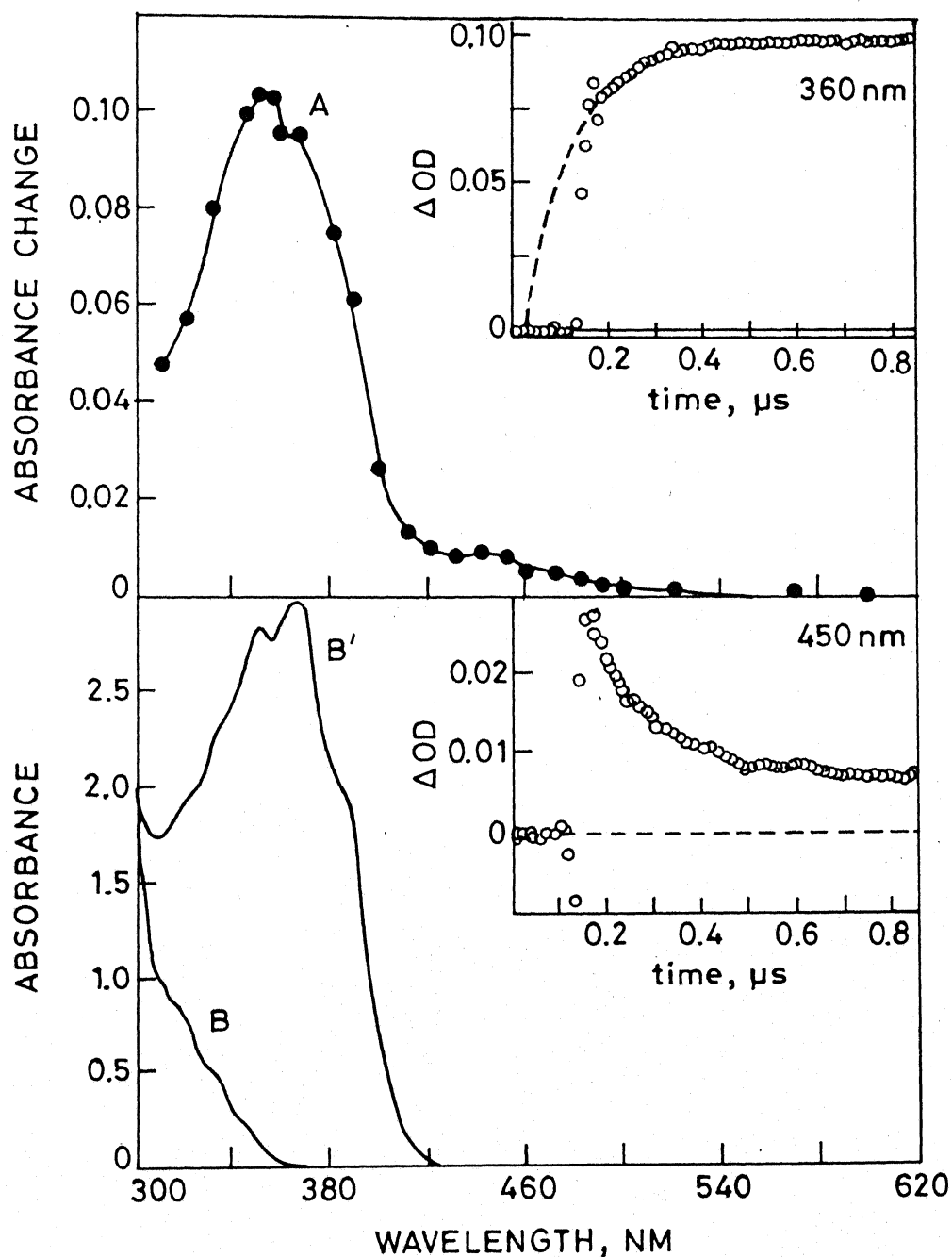


Fig. II.4 (A) Absorption spectra of photoproducts at 5 μs following 337.1 nm laser excitation of 23 in benzene. (B) Ground-state absorption spectrum of 23 in benzene. (B') Absorption spectra of photoproducts upon prolonged photolysis of 23 in benzene by repetitive 337.1 nm laser pulses. Insets: kinetic traces at the wavelengths indicated.

Equation 1 was used (BP = benzophenone,

$$\phi_P \epsilon_{\max}^P = \phi_{T,BP} \frac{\Delta OD_P}{\Delta OD_{T,BP}} \epsilon_{\max,BP}^T \quad (1)$$

P = photoproduct), wherein ΔOD_P designates the end-of-pulse absorbance change due to major transient at its wavelength maximum, except in the case of 23. For 23, absorbance changes at 360 nm following the completion of the growth process ($\tau = 110$ ns) were used for ΔOD_P to give $\phi_P \epsilon_{\max}^P$ values 1.7×10^4 and $1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in benzene and methanol, respectively. The spectral and kinetic data concerning the major transient in the case of 1a,b, 21a,b, 22 and 25-27 are summarized in Table II.1.

b) Triplet Sensitization Studies. In order to establish that the major transients seen upon direct laser excitation of the aziridines were formed under triplet sensitization also, pulse radiolysis experiments were carried out for 1a,b, 21a and 23 in benzene with acetophenone as the sensitizer. In these experiments, acetophenone was present at a relatively high concentration (0.08-0.1 M) and acted as the primary acceptor of energy from pulse-radiolytically generated solvent (benzene) triplets.²³⁻²⁵ In the presence of benzoylaziridine substrates (1-5 mM), the triplet energy was subsequently transferred from the acetophenone triplet to the substrates and the formation of triplet-derived photoproducts was observed. The transient spectra and some representative kinetic traces are presented in Figure II.5. The spectral and kinetic behaviour of the transients ($\lambda_{\max} = 475\text{-}480$ nm) with 1a,b and 21a as

TABLE II.1 Absorption-Spectral and Kinetic Data for Major Transients, Photogenerated from Benzoylaziridines at Room Temperature^a

sub- strate	solvent	λ_{\max} , ^b	$\phi \epsilon_{\max}^P$, ^c $10^3 M^{-1} cm^{-1}$	τ , ^d μs
<u>1a</u>	benzene	475	3.1	1.9
	methanol	450	2.5	55 (5.8)
<u>1b</u>	benzene	475	4.8	2.4
	methanol	450	3.0	63 (10)
<u>21a</u>	benzene	480	9.8	>500
	methanol	480	10.1	17 ^e (>500) ^f
<u>21b</u>	benzene	485	9.0	>500
	methanol	480	13.3	21 ^e (>500) ^f
<u>22</u>	benzene	480	11.2	>500
	methanol	480	11.3	34 ^e (>500) ^f
<u>25</u>	benzene	475	2.6	3.3
	methanol	450	1.7	170 (10)
<u>26</u>	benzene	460	5.8	3.4
	methanol	455	4.4	73 (8.7)
<u>27</u>	benzene	470	5.3	2.5
	methanol	455	6.7	54 (5.5)

^a Laser excitation wavelength, 337.1 nm. ^b ± 5 nm. ^c $\pm 15\%$.

^d $\pm 15\%$; the data in parenthesis are in acetonitrile. ^e Lifetimes for growth of transient absorption at λ_{\max} in methanol. ^f Lifetimes measured by conventional lamp flash photolysis in acetonitrile are 30, 45 and ~ 300 ms for major transients derived from 21a, 21b and 22, respectively.

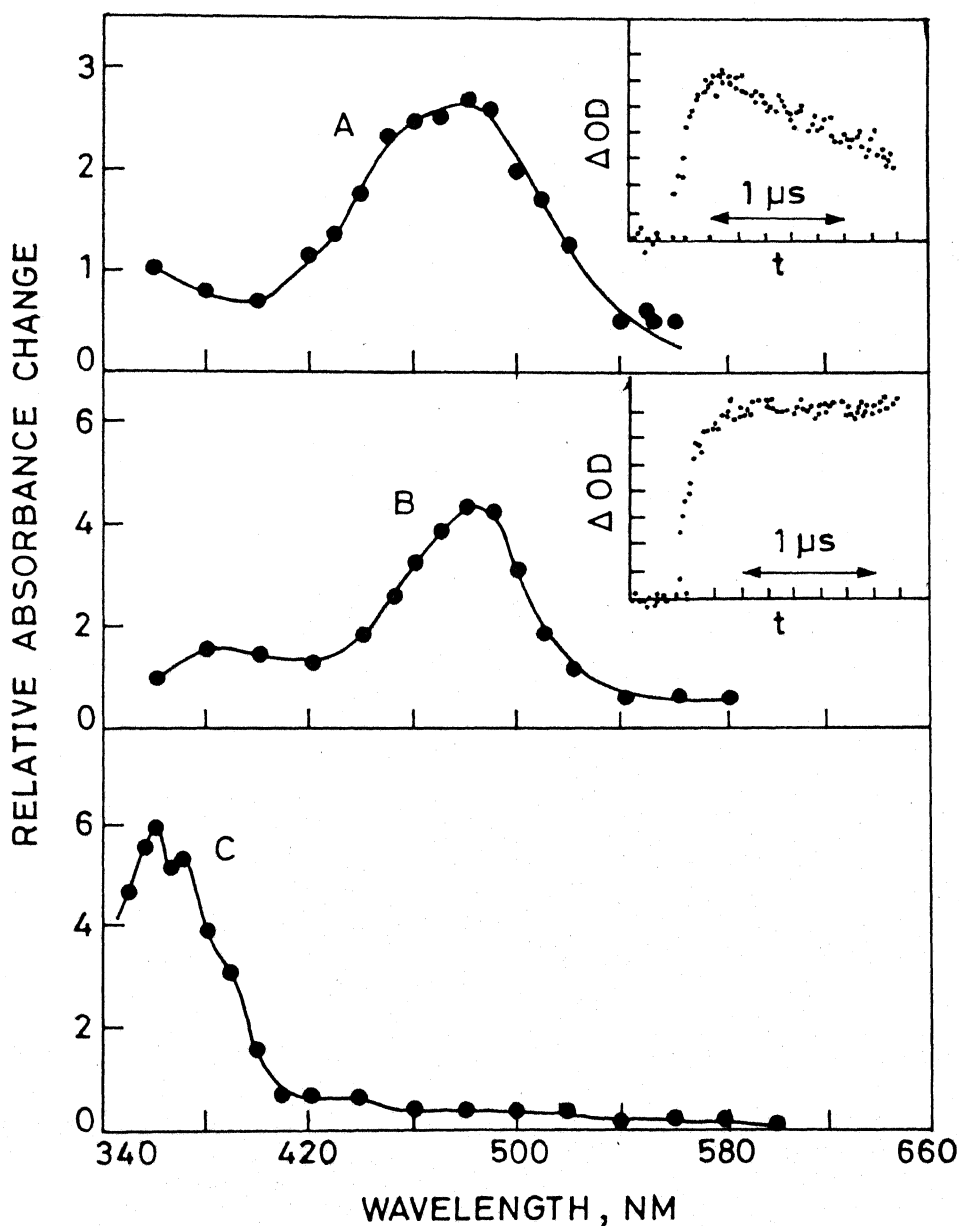


Fig. II.5 Transient absorption spectra observed upon pulse radiolysis of 0.1M acetophenone in the presence of (A) 3.3 mM 1a , (B) 1.1mM 21a , and (C) 1.2mM 23 in benzene at 10 μs following the electron pulse. Insets: kinetic traces at 480 nm for (a) 1a and (b) 21a .

the substrates, and the permanent product ($\lambda_{\text{max}} = 360 \text{ nm}$) with 23 as the substrate, under sensitization by pulse-radio-lytic acetophenone triplet were very similar to those observed under direct laser excitation (described earlier).

The 2-aryl-3-arylaziridines 1b, 23 and 26 have relatively small ground state extinction coefficients at 337.1 nm. With these substrates, triplet-sensitization experiments were carried out by laser flash photolysis using acetophenone as the sensitizer in benzene, with the latter being preferentially excited at 337.1 nm. The transient kinetics and absorption spectra, under these conditions, were no different from those observed under direct laser excitation.

c) Probing Biradicals and Carbonyl Triplet Precursors.

The involvement of short-lived carbonyl triplets has been probed by conventional probes such as dienes and naphthalene derivatives.²⁶ We have examined the quenching effect of DMHD (added up to 0.35 M) upon the end-of-pulse absorbance changes (ΔOD) due to major photoproducts arising from laser pulse excitation (337.1 nm) of each of the substrates in benzene. The most pronounced effects were observed for 21b, 23 and 27. Stern-Volmer plots based on equation 2

$$\frac{\Delta OD_0}{\Delta OD} = 1 + k_q^T \tau_T [\text{DMHD}] \quad (2)$$

for these substrates are shown in Figure II.6. Since the plots are essentially linear, one carbonyl triplet precursor appears to be predominant in each case. Estimates of $k_q^T \tau_T$ are given in Table II.2.

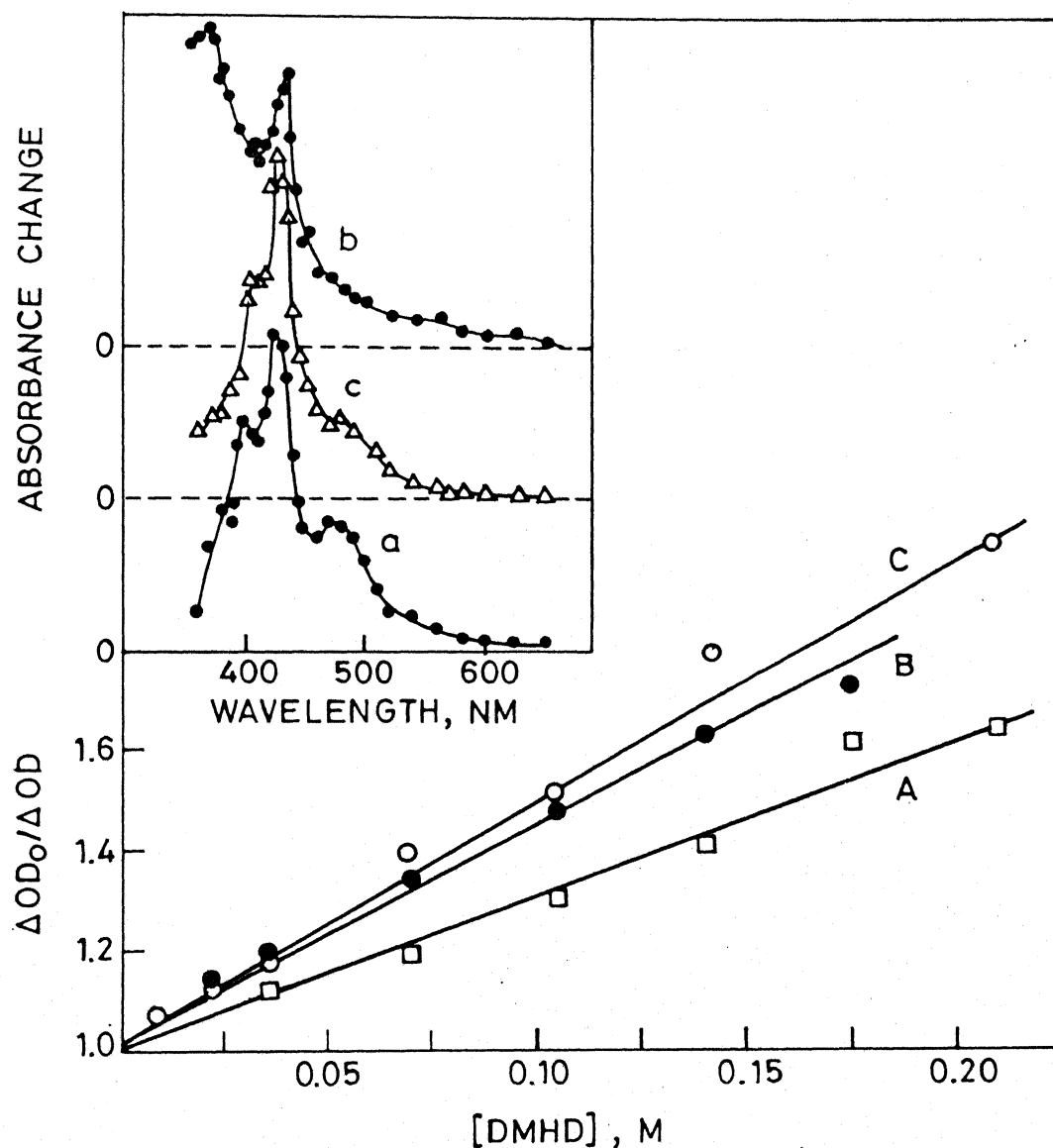


Fig. II.6 Stern-Volmer plots for DMHD quenching of ylide yield based on equation 2 with (A) 21b, (B) 23 and (C) 27 in benzene. Inset: the transient spectra at 0.2 μ s following 337.1 nm laser excitation of (a) 21b, (b) 23 and (c) 27 in the presence of 0.42 M MN in benzene.

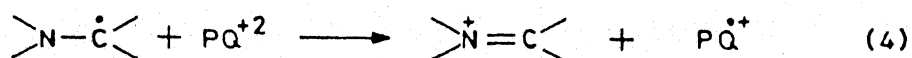
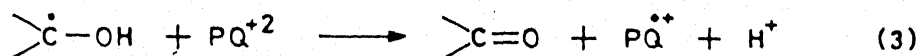
TABLE II.2 Slopes of Stern-Volmer Plots for DMHD Quenching
of Major Transient ^a Yields in Benzene ^b

substrate	$k_q^T \tau_T^c, M^{-1}$	τ_T^d, ns
<u>1a</u>	≤ 0.5	≤ 0.1
<u>1b</u>	~ 0.9	~ 0.2
<u>21a</u>	< 0.5	< 0.1
<u>21b</u>	4.8 (4.8)	1.0
<u>22</u>	≤ 0.5	≤ 0.1
<u>23</u>	2.9	0.6
<u>25</u>	~ 0.8	~ 0.2
<u>26</u>	~ 0.8	~ 0.2
<u>27</u>	4.4 (3.8)	0.9

^a Except 23 for which absorbance changes due to the permanent photoproduct at 360 nm were monitored. ^b Laser excitation wavelength, 337.1 nm. ^c $\pm 20\%$; the data in parentheses are from MN quenching. ^d Based on $k_q^T = 5 \times 10^9 M^{-1} s^{-1}$ for triplet energy transfer from carbonyl triplets to DMHD in benzene.

Involvement of short-lived triplets, quenchable by 1-methylnaphthalene (MN) under direct excitation was also shown by the laser flash photolysis of 21b, 23 and 27 in the presence of 0.1–0.7 M MN in benzene. The transient spectra given in the inset of Figure II.6, attest the formation of MN triplet with its sharp absorption maximum at 425 nm. Laser flash photolysis of optically matched benzene solutions of 21b and 27 and benzophenone (reference) in the presence of 0.1–0.7 M MN and comparison of the intercepts of the plots of the reciprocal of triplet absorbance due to $^3\text{MN}^*$ at 425 nm against $1/[\text{MN}]$ gave estimates of triplet yields (ϕ_T) as 0.8 ± 0.1 and 0.7 ± 0.1 for 21b and 27, respectively (in benzene, relative to benzophenone).

Intramolecular hydrogen transfer in the excited states of benzoylaziridines should lead to biradicals containing ketyl and aminoalkyl radical moieties, both of which are readily oxidizable^{27,28} by paraquat (1,1'-dimethyl-4,4'-bipyridinium dication, PQ^{+2}). The reactions (equations 3 and 4) are well recognized in the literature^{27–34} and have often been used^{29,30} to probe biradicals of Norrish type II photoreactions.



Laser flash photolysis (337.1 nm) of methanolic solutions of 23, 25 and 27, containing 2–20 mM $[\text{PQ}^{+2}]$ showed appreciable formation of $\text{PQ}^{\bullet+}$, with its characteristic absorption maxima

at 395 (sharp) and 610 nm (broad) (see the inset of Figure II.7). With other substrates, $PQ^{\bullet+}$ formation was small and can be accounted for, to a large extent, by the fractional absorption of laser photons by PQ^{+2} itself, leading to its photoreduction.^{35,36} Using optically matched solutions (OD = 1.0 in 2 mm cell at 337.1 nm) of 23, 25, 27 and 4,4'-dimethoxybenzene in methanol, absorbance change ($\Delta OD_{PQ^{\bullet+}}$) due to $PQ^{\bullet+}$ at 610 nm was measured as a function of $[PQ^{+2}]$. Double-reciprocal plots of $\Delta OD_{PQ^{\bullet+}}$ against $[PQ^{+2}]$, based on equation 5, are shown in Figure II.7. The linearity of these plots suggests that a single photointermediate (biradical), oxidizable

$$\frac{1}{\Delta OD_{PQ^{\bullet+}}} = \text{Const} \times \left(1 + \frac{1}{k_q^B \tau_B [PQ^{+2}]} \right) \quad (5)$$

by PQ^{+2} is involved in each case. Values of $k_q^B \tau_B$, measured from the intercept-to-slope ratios and quantum yields (ϕ_B) of biradicals estimated from the comparison of intercepts with that in the case of 4,4'-dimethoxybenzophenone triplet (electron donor),²⁷ are presented in Table II.3.

In the case of 23, the decay of the fast component of transient absorption at 400-550 nm became enhanced in the presence of PQ^{+2} , suggesting that the short-lived species responsible for this decay process was the reductant for PQ^{+2} . The plot of the pseudo-first-order rate constant for $PQ^{\bullet+}$ formation against $[PQ^{+2}]$ gave $(4.7 \pm 0.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as the rate constant for electron transfer to paraquat, the intercept ($\sim 1.0 \times 10^7 \text{ s}^{-1}$) of this plot is close to the rate constant,

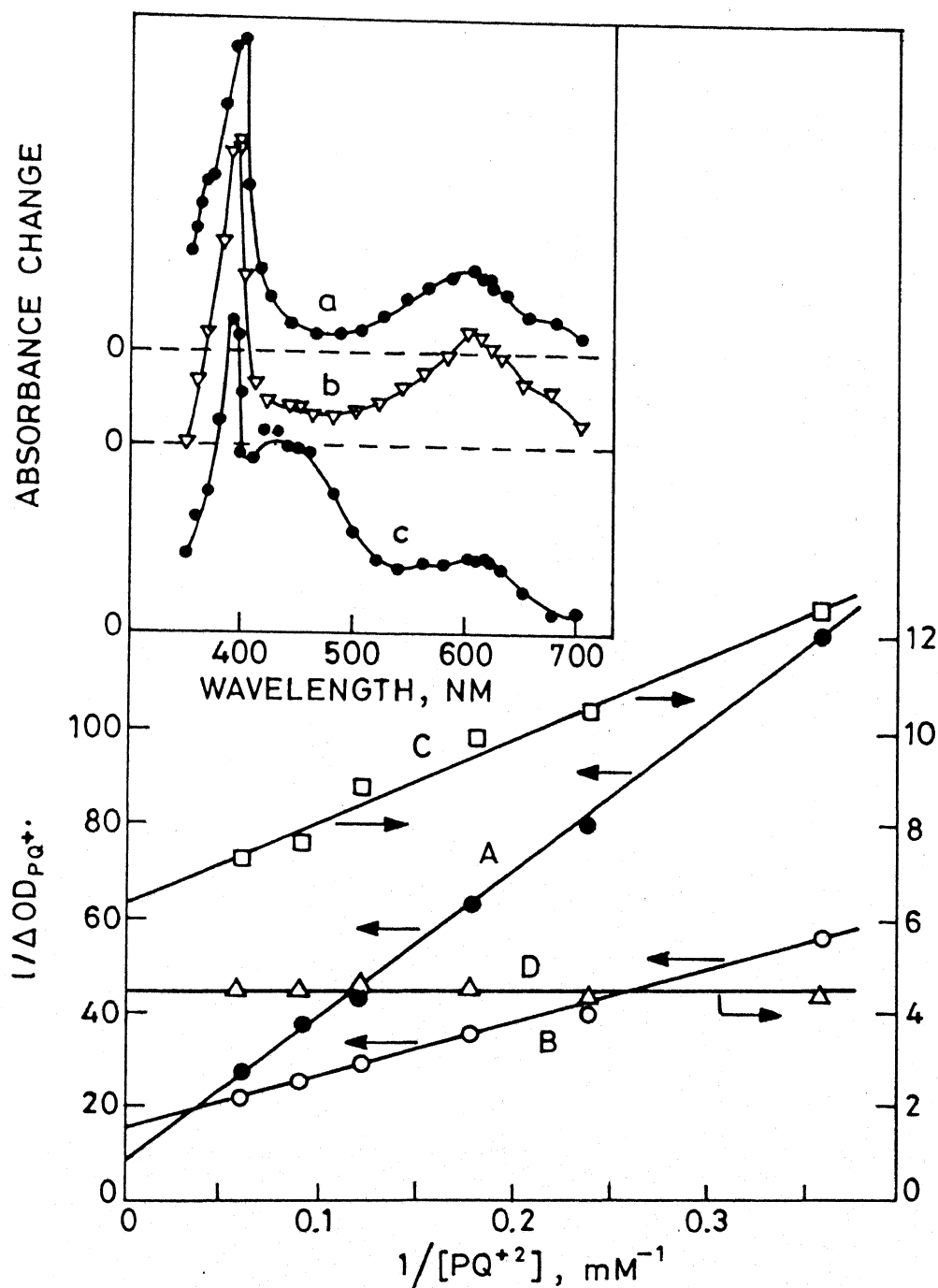


Fig. II.7 Plots, based on equation 5, for the absorbance change due to $PQ^{+•}$ (at 610 nm) formed as a result of 337.1 nm laser excitation of (A) 23, (B) 25, (C) 27 and (D) 4, 4'-dimethoxybenzophenone in methanol. Insets: the transient spectra at 0.5 μs following 337.1 nm laser excitation of (a) 23, (b) 25, and (c) 27 in the presence of 18 mM PQ^{+2} in methanol.

TABLE II.3 $k_q^B \tau_B$ and ϕ_B Data ^a Obtained from Paraquat
Reduction in Methanol ^b

substrate	ϕ_B	$k_q^B \tau_B, M^{-1}$	$\tau_B, \overset{c}{\text{ns}}$
<u>23</u>	0.7 ± 0.1	400 ± 50	85
<u>25</u>	0.3 ± 0.1	127 ± 20	27
<u>27</u>	0.5 ± 0.1	30 ± 6	6

^a Average of three measurements. ^b Laser excitation wavelength; 337.1 nm. ^c Based on $k_q^B = 4.7 \times 10^9 M^{-1} s^{-1}$.

$(9.0 \pm 0.8) \times 10^6 \text{ s}^{-1}$, observed for the decay of the fast component in the case of 23 (in the absence of a quencher). Also, note that the $k_q \tau$ value (470 M^{-1}) calculated from $\text{PQ}^{\bullet+}$ growth kinetics and the $k_q^B \tau_B$ value (400 M^{-1}) obtained from the treatment of $\text{PQ}^{\bullet+}$ absorbance data, based on equation 5 agree with each other within experimental error. All these results point to an assignment of the 110 ns transient in the case of 23 as a biradical and acts as a precursor for the 360 nm permanent product. Assuming a value of $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_q^B for biradical intermediates in the case of 25 and 27, τ_B 's were estimated to be 27 and 6 ns, respectively.

d) Quenching of the Major Transient ($\lambda_{\text{max}} = 440\text{-}480 \text{ nm}$) by Acids and DMAD. The decay of the major transient of aziridines absorbing at 440-480 nm was found to be very sensitive to trifluoro- and trichloroacetic acids, suggesting a zwitterionic nature and high proton affinity. Unfortunately, the acid quenching study was complicated due to the protonation of the aziridine substrates in the ground state. Nevertheless, the following observations deserve mention. First, at a given substrate concentration (0.05-0.1 M) in benzene, the rate constant for transient quenching in the case of 1a was 4-6 times smaller than that in the case of 1b, suggesting that the transients photogenerated from these two isomeric aziridines are distinct. A similar but smaller difference could be observed in the case of the isomeric aziridines 21a and 21b also. In this case, however, the transient from the cis-aziridine 21b was less reactive.

The 1,3-dipolar addition of azomethine ylides to dipolarophiles (ethylene/acetylene derivatives) under conditions of both thermolysis and photolysis of aziridines is well established in the literature.^{11-15,37-40} Thus, a convincing support for the ylide assignment was sought from the quenching effect of a typical dipolarophile. Attempts to quench the 440-480 nm transients by DMAD at millimolar concentrations showed very little or no enhancement in their decay over 20-150 μ s. Since the dibenzoylaziridines 21a,b and 22 give transients ($\lambda_{\text{max}} \sim 480$ nm) that are very longlived, conventional lamp flash photolysis experiments were carried out for these systems in acetonitrile. The lifetimes of the transients were found to be 30-300 ms in this solvent, and the enhancement of their decay was readily observed upon addition of 5-50 mM DMAD. The bimolecular rate constants for transient quenching of these substrates by DMAD in acetonitrile and a rough estimate of the same for 1a,b and 25-27 in methanol are presented in Table II.4.

e) Assignment of Major Transients. The most plausible interpretation for the major transient species ($\lambda_{\text{max}} = 450-480$ nm) photogenerated from 1a,b, 21a,b, 22 and 25-27 appears to be azomethine ylides formed via C-C bond cleavage in the aziridine ring. This assignment is based on the similarity of spectral features with those of stable coloured species, formed upon photolysis at 77 K and on the quenching behaviour toward acids and DMAD. Assignments in terms of long-lived triplets or triplet biradicals (derived from intramolecular hydrogen abstraction or C-N bond cleavage in the aziridine ring) are ruled out

TABLE II.4 Rate Constants (k_q) for Major Transient Quenching by DMAD

substrate	solvent	max [DMAD], M	k_q , ^a $10^3 \text{ M}^{-1} \text{ s}^{-1}$
<u>1a</u>	methanol	2.7	<u>≤5</u>
<u>1b</u>	methanol	2.3	<u>≤8</u>
<u>21a</u>	acetonitrile	0.041	3.2
<u>21b</u>	acetonitrile	0.048	2.9
<u>22</u>	acetonitrile	0.048	0.86
<u>25</u>	methanol	2.3	<u>≤6</u>
<u>26</u>	methanol	2.3	<u>≤5</u>
<u>27</u>	methanol	2.3	<u>≤15</u>

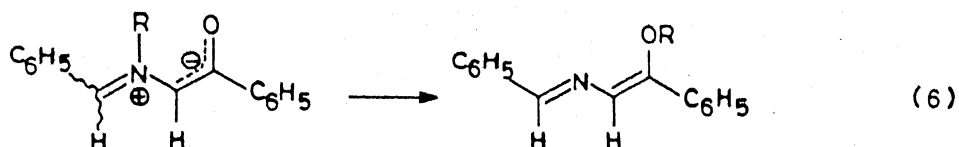
^a Measured for benzoylaziridines 1a,b and 25-27 by 337.1 nm laser flash photolysis (transient decay observed at 450 nm over 150 μs) and for dibenzoylaziridines 21a,b and 22 by conventional lamp flash photolysis (transient decay observed at 480 nm over 0.1-1 s).

both 21a and 21b in the presence of DMAD gave similar mixtures of products consisting of the pyrroline 61, the pyrrole 63 and the two unidentified compounds (Scheme II.7). It may be noted that acid-quenching studies (see earlier) had suggested that the azomethine ylides photogenerated from 21a and 21b are distinct. This is taken to mean that the pyrrolines formed (stereospecifically) undergo epimerization under the conditions of workup to give the more stable (thermodynamically)¹⁵⁻¹⁷ cis-pyrroline 61. Since the cis-trans isomerization of aziridines is not observed, isomerization of the azomethine ylide itself, may be ruled out.

As evident from the data presented in Table II.1, among the methyl/methoxy-substituted benzoylaziridines, the substituents do not have any drastic effect on ylide lifetimes and absorption maxima. However, between a benzoylaziridine (e.g., 1a) and a dibenzoylaziridine (e.g., 21a), the following two differences are evident. First, in methanol the λ_{max} is red-shifted by ~30 nm in the case of dibenzoylaziridine. Second, the azomethine ylide photogenerated from 21a is considerably longer-lived than that from 1a. Based on electronic effects, one would expect the absorption spectra of ylides from benzoylaziridines to be red-shifted and the ylide itself to be longer-lived. The observation to the contrary may be explained in terms of less steric distortion from planarity in the case of ylides, photogenerated from dibenzoylaziridines.

The parallelism in kinetics of growth processes at short wavelengths (300-360 nm) with those of the decay of ylides in

various solvents in the presence or absence of ylide quenchers suggests that the former are the results of thermal changes associated with ylides. One process that seems plausible is the 1,4-migration^{40,42-44} of the substituent on the nitrogen atom to the carbonyl oxygen, forming a 1,4-diphenylbutadiene analogue (equation 6), which should absorb strongly at 320-360 nm.



The permanent photoproduct ($\lambda_{\text{max}} = 360 \text{ nm}$) observed in the case of 23 may be the 1,4-butadiene analogue 42 (Scheme II.5), formed through the intermediacy of biradical 39 ($\tau = 110 \text{ ns}$). The assignment is based on the isolation of benzaldehyde (37) and the pyrazine 49. The azomethine ylide in this case, is a minor product and probably corresponds to the tail absorption (transient) of 400-500 nm observed in the course of low-temperature photolysis in the glass, as well as laser flash photolysis in fluid solutions.

The quenching studies with DMHD and MN clearly establish that very short-lived carbonyl-type triplets act as precursors for the 360 nm species in the case of 23 and for azomethine ylides in the case of most of the other benzoylaziridines. The triplet involvement is also supported by sensitization studies with acetophenone as the triplet donor. For 21b, 23 and 27, the triplets are relatively long-lived ($\tau_T \approx 1 \text{ ns}$). Note that these are the substrates in which intramolecular hydrogen abstraction is

less favourable due to electronic effects and/or structural constraints. In analogy to the mechanism⁴⁵⁻⁴⁸ of bimolecular quenching of ketone triplets by amines, one would expect intramolecular electron transfer, forming an exciplex ($^3E^*$), to precede the proton transfer (recognized by Padwa and coworkers).⁶⁻¹⁰ In such a case, the difficulty of proton transfer in $^3E^*$ determines its lifetime. To explain the trend in τ_T 's, estimated from diene quenching, an equilibrium between $^3E^*$ and locally excited carbonyl triplet (T_1^*) has to be invoked.

Among the substrates under study, particularly, 23, 25 and 27 show the involvement of a relatively long-lived biradical, oxidizable by PQ^{+2} . These are best assigned as the biradicals formed by intramolecular hydrogen transfer and C-N bond cleavage (see Schemes II.1-II.6). Thus, short lifetimes of biradicals suggest that the rupture of the weak bond(s) in the strained aziridine ring provides a thermodynamically favourable pathway for fast degradation of the biradicals to products.

f) Comparison with Benzoyloxiranes. The comparison of the properties of azomethine ylides photogenerated from benzoylaziridines with those of carbonyl ylides photogenerated from benzoyloxiranes⁴⁹ forms an interesting study. Substituent effects on absorption maxima and decay kinetics of carbonyl ylides, for example, are pronounced and systematic, compared to those in the case of azomethine ylides. The carbonyl ylides are short-lived ($\tau \approx 50-170 \mu s$ in methanol) and have their

maxima considerably red-shifted ($\lambda_{\text{max}} = 520\text{--}600\text{ nm}$). The reactivity of carbonyl ylides with DMAD is 10^5 times faster than that of azomethine ylides. Alcohols prove to be ready reactant (quencher) for the carbonyl ylides, while the azomethine ylides apparently become stabilized in the presence of alcohols. Carbonyl triplets are shown to be involved as ylide precursors for both classes of benzoyl derivatives, they are far more short-lived ($\tau_T \leq 1\text{ ns}$) in the case of aziridines; this reflects the importance of intramolecular electron transfer from the nitrogen center.

II.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or 580 infrared spectrometers. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. The ^1H NMR spectra were recorded on Varian EM-390 or Nicolet NB-300 NMR spectrometer, using tetramethysilane as internal standard. The mass spectra were recorded on a JEOL JMS-D 300 mass spectrometer at 70 eV. All steady-state irradiations were carried out either in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR, 2537 or 3000 Å) or by using a Hanovia 450 W medium pressure mercury lamp in a quartz-jacketted immersion well or using the output (3660, 3350, 3150 Å) from medium pressure Hg lamp (B and L SP-200) coupled with a monochromator (B and L 33-86-07).

II.4.1 Starting Materials. trans-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (1a),⁵⁰ mp 101-102 °C, cis-1-cyclohexyl-2-phenyl-3-benzoylaziridine (1b),^{51,52} mp 105-106 °C, trans-1-cyclohexyl-2,3-dibenzoylaziridine (21a),⁵³ mp 138-139 °C, cis-1-cyclohexyl-2,3-dibenzoylaziridine (21b),⁵³ mp 148-149 °C, trans-1-benzyl-2,3-dibenzoylaziridine (22),⁵³ mp 134-135 °C, trans-2-phenyl-3-benzoylaziridine (23),⁵⁰ mp 99-100 °C, trans-1,3-dibenzoyl-2-phenylaziridine (24),⁴² mp 128-129 °C, trans-1-cyclohexyl-2-p-anisyl-3-benzoylaziridine (25),^{54,55} mp 90-91 °C, cis-1-cyclohexyl-2-p-tolyl-3-benzoylaziridine (26),⁵⁶ mp 122 °C, cis-1-cyclohexyl-2-phenyl-3-anisoylaziridine (27),⁵⁶ mp 173-174 °C and dimethyl acetylenedicarboxylate (DMAD),⁵⁷ bp 95-98 °C/19 mm were prepared by reported procedures. 1-Methylnaphthalene (MN), 2,5-dimethyl-2,4-hexadiene (DMHD) and trichloroacetic acid used were obtained from Aldrich. Paraquat (PQ²⁺, methylviologen, Aldrich) was precipitated from aqueous methanol by adding excess of acetone. Petroleum ether used was the fraction with bp 60-80 °C.

II.4.2 Photolysis of trans-1-Cyclohexyl-2,3-dibenzoylaziridine (21a). A solution of 21a (500 mg, 1.5 mmol) in benzene (300 mL) was irradiated (RPR, 3000 Å) for 4 h at ca. 25 °C. The experiment was repeated to photolyse, in all 1.0 g (3.0 mmol) of 21a. Removal of the solvent under vacuum gave a residual solid, which was separated by preparative thin layer chromatography over silica gel to give 520 mg (52%) of (Z)-1-Cyclohexylamino-1,2-dibenzoylethylene (31),⁵³ mp 131-132 °C (mixture

mp), after recrystallization from petroleum ether and 360 mg (36%) of the unchanged 21a, mp 138-139 °C (mixture mp).

II.4.3 Photolysis of cis-1-Cyclohexyl-2,3-dibenzoyl-aziridine (21b). A solution of 21b (500 mg, 1.5 mmol) in benzene (300 mL) was irradiated (RPR, 3000 Å) for 6.5 h at ca. 25 °C. The irradiation experiment was repeated to photolyse, in all 1.0 g (3.0 mmol) of 21b. Removal of the solvent under reduced pressure gave a product mixture, which was separated by preparative thin layer chromatography over silica gel to give 320 mg (32%) of 31, mp 131-132 °C (mixture mp) and 540 mg (54%) of the unchanged 21b, mp 148-149 °C (mixture mp).

II.4.4 Photolysis of trans-1-Benzyl-2,3-dibenzoyl-aziridine (22). A solution of 22 (511 mg, 1.5 mmol) in benzene (300 mL) was irradiated (RPR, 3000 Å) for 4 h at ca. 25 °C. The photolysis was repeated to photolyse, in all 1.022 g (3.0 mmol) of 22. Removal of the solvent under vacuum gave a product mixture, which was separated by preparative thin layer chromatography over silica gel to give trans-dibenzoylethylene (36, 50 mg, 7%), mp 110-111 °C (mixture mp), benzaldehyde (37, 32 mg, 6%), (superimposable ir spectrum with that of an authentic sample) and 800 mg (80%) of (Z)-1-benzylamino-1,2-dibenzoylethylene (38),⁵³ mp 102-103 °C (mixture mp), after recrystallization from petroleum ether.

II.4.5 Photolysis of trans-2-Phenyl-3-benzoylaziridine (23). A solution of 23 (446 mg, 2.0 mmol) in benzene (350 mL) was irradiated (Hanovia 450 W, medium pressure Hg lamp) for

4.5 h at ca. 25 °C. The photolysis was repeated to photolyse, in all 2.23 g (10.0 mmol) of 23. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 35 mg (3%) of acetophenone (47) (superimposable ir spectrum with that of an authentic sample). Continued elution with a mixture (3:7) of benzene and petroleum ether gave 64 mg (6%) of benzaldehyde (37) (superimposable ir spectrum with that of an authentic sample). Further elution with a mixture (1:1) of benzene and petroleum ether gave 93 mg (8%) of 2,5-diphenylpyrazine (49), mp 193-194 °C (lit.²⁰ mp 191-193 °C), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Continued elution with benzene gave 240 mg (11%) of 2,5-dibenzoyl-3,6-diphenylpyrazine (48), mp 145-146 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3045, 3020, 2950, 2920 (CH), 1660 (C=O), 1590 and 1580 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 253 nm (ϵ , 62,000) and 296 (46,000).

^1H NMR spectrum (CDCl_3): δ 7.23-8.03 (m, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 127.12, 128.36, 128.63, 128.69, 128.76, 129.03, 129.12, 129.25, 129.49, 129.87, 130.19, 130.51, 133.77, 134.04, 135.78, 136.07, 141.45, 149.29 and 193.58 (C=O).

Mass spectrum, m/e (relative intensity): 440 (M^+ , 1), 336 ($M^+ - \text{COC}_6\text{H}_4$, 99), 335 ($M^+ - \text{COC}_6\text{H}_5$, 26), 307 ($M^+ - \text{COC}_6\text{H}_5$, - CO, 39), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2$: C, 81.81; H, 4.54; N, 6.36. Found: C, 81.63; H, 4.68; N, 6.12.

Further elution of the column with benzene gave 710 mg (32%) of the unchanged 23, mp 99-100 °C (mixture mp). Continued elution with a mixture (9:1) of benzene and ethyl acetate gave 45 mg (4%) of benzamide (46), mp 131-132 °C (mixture mp). Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 200 mg (9%) of dihydropyrazine 44, mp 228-229 °C (lit.⁴² mp 232-234 °C).

Conversion of 44 to 48. To a solution of 44 (110 mg, 0.25 mmol) in benzene (5 mL) was added freshly prepared nickel peroxide (90 mg, 1.0 mmol) and the reaction mixture was stirred for 40 h at ca. 25 °C. The inorganic material was removed by filtration and removal of the solvent from the filtrate, under vacuum gave 75 mg (68%) of 48, mp 145-146 °C (mixture mp), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

II.4.6 Photolysis of trans-1,3-Dibenzoyl-2-phenylaziridine (24). A solution of 24 (327 mg, 1.0 mmol) in benzene (300 mL) was irradiated (RPR, 3000 Å) for 2 h at ca. 25 °C. The experiment was repeated to photolyse, in all 981 mg (3.0 mmol) of 24. Removal of the solvent under vacuum gave a

product mixture, which was chromatographed over neutral alumina. Elution with petroleum ether gave 80 mg (12%) of 2,5-diphenyloxazole (17), mp 80-81 °C (mixture mp), after recrystallization from petroleum ether. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 170 mg (46%) of benzoic acid (55), mp 120-121 °C (mixture mp). Further elution of the column with benzene gave 350 mg (52%) of trans-2-phenyl-3-benzoylaziridine (23), mp 99-100 °C (mixture mp). Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 80 mg (8%) of benzamide (46), mp 131-132 °C (mixture mp).

In a separate experiment, a solution of 24 (100 mg, 0.3 mmol) in methylene chloride (10 mL) was treated with neutral alumina (1.0 g) and stirred at ca. 25 °C for 2 h. Removal of the inorganic material by filtration and the solvent under vacuum gave 65 mg (96%) of 23, mp 99-100 °C (mixture mp).

II.4.7 Photolysis of a Mixture of trans-1-Cyclohexyl-2-Phenyl-3-benzoylaziridine (1a) and Dimethyl Acetylenedicarboxylate (DMAD). A mixture of 1a (1.0 g, 3.27 mmol) and DMAD (0.93 g, 6.55 mmol) in acetonitrile (350 mL) was irradiated (Hanovia 450 W, medium pressure Hg lamp) for 1 h at ca. 15-20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over florisil. Elution of the column with a mixture (9:1) of benzene and petroleum ether gave 0.4 g of the unchanged DMAD, bp 95-98 °C/19 mm. Continued elution with benzene gave 380 mg (26%)

of dimethyl 1-cyclohexyl-2-phenyl-5-benzoylpyrrole-3,4-dicarboxylate (58),⁴ mp 142-143 °C (mixture mp), after recrystallization from methanol. Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 750 mg (51%) of dimethyl trans-1-cyclohexyl-2-phenyl-5-benzoyl-3-pyrroline-3,4-dicarboxylate (57a), as a viscous liquid.

IR spectrum ν_{\max} (neat): 3080, 3050, 3020, 2960, 2850 (CH), 1715, 1680 (C=O), 1590 and 1570 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 225 nm (ϵ , 44,000), 268 (29,500), and 284 (3,500).

¹H NMR spectrum (CDCl_3): δ 0.75-2.38 (11 H, m, cyclohexyl), 3.32 (1 H, s, methine), 3.63 (1 H, s, methine), 3.75 (3 H, s, methoxy), 3.92 (3 H, s, methoxy), and 7.08-7.95 (10 H, m, aromatic).

Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_5$: C, 72.48; H, 6.48; N, 3.13. Found: C, 72.03; H, 6.27; N, 3.27.

Conversion of 57a to 58. A solution of 57a (200 mg, 0.44 mmol) in benzene (10 mL) was saturated with oxygen and refluxed for 5 h. Removal of the solvent under vacuum gave 190 mg (96%) of 58, mp 142-143 °C (mixture mp), after recrystallization from methanol.

II.4.8 Photolysis of a Mixture of cis-1-Cyclohexyl-2-phenyl-3-benzoylaziridine (1b) and Dimethyl Acetylenedicarboxylate (DMAD). A mixture of 1b (1.0 g, 3.27 mmol) and DMAD (0.93 g, 6.55 mmol) in acetonitrile (350 mL) was -

irradiated (Hanovia 450 W, medium pressure Hg lamp) for 3 h at ca. 15-20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave 0.45 g of the unchanged (DMAD), bp 95-98 °C/19 mm. Further elution with a mixture (1:1) of benzene and petroleum ether gave 50 mg (3%) of dimethyl 1-cyclohexyl-2-phenylpyrrole-3,4-dicarboxylate (59b), ⁵⁸ mp 109-110 °C, after recrystallization from petroleum ether. Continued elution with benzene gave 200 mg (20%) of the unchanged 1b, mp 105-106 °C (mixture mp). Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 1.05 g (62%) of dimethyl cis-1-cyclohexyl-2-phenyl-5-benzoyl-3-pyrroline-3,4-dicarboxylate (57b), as a viscous liquid.

IR spectrum ν_{\max} (neat): 3080, 3045, 3020, 2940, 2850 (CH), 1715, 1665 (C=O), 1600 and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 228 nm (ϵ , 45,500), 265 (27,700), and 278 (1,800).

¹H NMR spectrum (CDCl₃): δ 0.83-1.78 (11 H, m, cyclohexyl), 3.18 (1 H, s, methine), 3.48 (1 H, s, methine), 3.53 (3 H, s, methoxy), 3.70 (3 H, s, methoxy), and 7.13-7.95 (10 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 447 (M^+ , 1), 342 ($M^+ - \text{COC}_6\text{H}_5$, 18), 341 ($M^+ - \text{C}_6\text{H}_5\text{CHO}$, 100), 310 ($M^+ - \text{C}_6\text{H}_5\text{CHO}$, - OCH_3 , 53), 259 ($M^+ - \text{C}_6\text{H}_5\text{CHO}$, - C_6H_{10} , 62), 228 ($M^+ - \text{C}_6\text{H}_5\text{CHO}$, - C_6H_{10} , - OCH_3 , 76), and other peaks.

Anal. Calcd for $C_{27}H_{29}NO_5$: C, 72.48; H, 6.48; N, 3.13.
Found: C, 72.16; H, 6.34; N, 3.48.

Conversion of 57b to 58. A solution of 57b (100 mg, 0.22 mmol) in benzene (5 mL) was refluxed for 10 h in the presence of oxygen. Removal of the solvent under vacuum gave the unchanged 57b (95 mg, 95%), (superimposable ir spectrum).

In a separate experiment, a mixture of 57b (200 mg, 0.44 mmol) and selenium dioxide (400 mg, 3.6 mmol) was heated at ca. 200 °C in a sealed tube for 1 h. The reaction mixture was extracted with methylene chloride and dried over anhydrous sodium sulphate. Removal of the solvent under vacuum gave a residue, which was recrystallized from methanol to give 160 mg (81%) of 58, mp 142-143 °C (mixture mp).

II.4.9 Photolysis of a Mixture of trans-1-Cyclohexyl-2,3-dibenzoylaziridine (21a) and Dimethyl Acetylenedicarboxylate (DMAD). A mixture of 21a (1.0 g, 3.0 mmol) and DMAD (0.85 g, 6.0 mmol) in acetonitrile (350 mL) was irradiated (Hanovia 450 W, medium pressure Hg lamp) for 45 min at ca. 15-20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave 0.33 g of the unchanged DMAD bp 95-98 °C/19 mm. Further elution with a mixture (2:3) of benzene and petroleum ether gave 100 mg (9%) of an unidentified compound (analysing to $C_{20}H_{18}O_6$), mp 189-190 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3080, 3058, 2995, 2940, 2830 (CH), 1725, 1665 (C=O) and 1588 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 222 nm (ϵ , 12,000), 258 (23,500), 290 (16,400), and 298 (15,000).

^1H NMR spectrum (CDCl_3): δ 3.75 (6 H, s, methoxy), 5.83 (2 H, s, vinylic), 7.58-7.97 (6 H, m, aromatic) and 8.18-8.56 (4 H, m, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 52.79 (q, methoxy), 53.14 (d, $\text{sp}^3\text{-C}$), 128.66, 129.35, 133.74, 136.21, 167.67 (C=O) and 193.77 (C=O).

Mass spectrum, m/e (relative intensity): 354 (11), 338 (7), 337 (62), 323 (8), 305 (17), 291 (78), 249 (9), 233 (18), 232 (99), 217 (12), 105 (100), 77 (98), and other peaks.

Anal. Found: C, 67.85; H, 5.18.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 25 mg (2%) of dimethyl 1-cyclohexyl-2-benzoylpyrrole-3,4-dicarboxylate (63), mp 109-110 $^{\circ}\text{C}$, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3075, 3000, 2940, 2860 (CH), 1730, 1720, 1640 (C=O), 1595 and 1575 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 244 nm (ϵ , 23,000), 250 (22,400), 256 (21,500) and 298 (12,500).

^1H NMR spectrum (CDCl_3): δ 1.08-2.33 (10 H, m, cyclohexyl), 3.23 (3 H, s, methoxy), 3.84 (3 H, s, methoxy), 4.23-

4.68 (1 H, m, α -proton of the cyclohexyl), and 7.28-7.93 (6 H, m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 369 (M^+ , 15), 338 ($M^+ - OCH_3$, 100), 307 ($M^+ - OCH_3$, 71), 224 ($M^+ - C_6H_{11}$, - OCH_3 , - OCH_3 , 40), 105 ($C_6H_5CO^+$, 40), and other peaks.

Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.29; H, 6.23; N, 3.79. Found: C, 68.45; H, 6.01; N, 3.75.

Continued elution with benzene gave 880 mg (62%) of dimethyl cis-1-cyclohexyl-2,5-dibenzoyl-3-pyrroline-3,4-dicarboxylate (61), as a viscous liquid.

IR spectrum ν_{max} (neat): 3066, 3045, 3000, 2950, 2938, 2860 (CH), 1730, 1685 (C=O), 1595 and 1580 (C=C) cm^{-1} .

UV spectrum λ_{max} (methanol): 225 nm (ϵ , 53,000), 258 (47,500), and 295 (18,000).

1H NMR spectrum ($CDCl_3$): δ 1.12-2.08 (11 H, m, cyclohexyl), 3.68 (2 H, s, methine), 3.85 (6 H, s, methoxy) and 7.15-8.30 (10 H, m, aromatic).

Anal. Calcd for $C_{28}H_{29}NO_6$: C, 70.73; H, 6.10; N, 2.98. Found: C, 71.15; H, 5.87; N, 2.68.

Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 132 mg (12%) of an unidentified compound (analysing to $C_{21}H_{23}NO_5$), mp 153-154 $^{\circ}C$, after recrystallization from a mixture (3:7) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3410 (OH), 3110, 3045, 2980, 2930, 2940 (CH), 1720, 1695 (C=O), 1600, 1575 and 1528 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 228 nm (ϵ , 47,600), 270 (27,000), and 273 (26,000).

^1H NMR spectrum (CDCl_3): δ 1.08-2.43 (10 H, m, cyclohexyl) 3.63 (3 H, s, methoxy), 3.69 (1 H, s, OH, D_2O -exchangeable), 3.88 (3 H, s, methoxy) and 7.20-7.68 (6 H, m, aromatic and vinylic).

^{13}C NMR spectrum (CDCl_3): δ 23.01 (t, $\text{sp}^3\text{-C}$), 23.22 (t, $\text{sp}^3\text{-C}$), 24.77 (t, $\text{sp}^3\text{-C}$), 32.03 (t, $\text{sp}^3\text{-C}$), 33.97 (t, $\text{sp}^3\text{-C}$), 51.25 (q, methoxy), 51.42 (q, methoxy), 84.25 (s, $\text{sp}^3\text{-C}$), 85.19 (s, $\text{sp}^3\text{-C}$), 108.79, 118.52, 122.59, 127.18, 128.08, 128.15, 128.35, 138.47, 144.62, 163.25 (C=O), and 164.17 (C=O).

Mass spectrum, m/e (relative intensity): 369 (7), 338 (18), 337 (46), 307 (7), 277 (10), 264 (100), 233 (12), 232 (65), 105 (67), and other peaks.

Anal. Found: C, 68.39; H, 6.25; N, 3.80.

Conversion of 61 to 62. To a solution of 61 (238 mg, 0.5 mmol) in benzene (15 mL) was added freshly prepared nickel peroxide^{59,60} (90 mg, 1 mmol) and the reaction mixture was stirred for 40 h. The inorganic material was removed by filtration and removal of the solvent from the filtrate under vacuum gave a residue, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give 180 mg (76%) of dimethyl 1-cyclohexyl-2,5-dibenzoylpyrrole-3,4-dicarboxylate

(62), mp 182-183 °C.

IR spectrum ν_{\max} (KBr): 3040, 3005, 2980, 2920 (CH), 1700, 1645 (C=O), 1585 and 1568 (C=C) cm^{-1} .

UV spectrum λ_{\max} (methanol): 227 nm (ϵ , 52,000), 262 (62,300), 267 (62,500) and 300 (31,500).

^1H NMR spectrum (CDCl_3): δ 0.93-2.13 (11 H, m, cyclohexyl), 3.31 (6 H, s, methoxy), and 7.33-8.21 (10 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 473 (M^+ , 3), 442 ($\text{M}^+ - \text{OCH}_3$, 6), 441 ($\text{M}^+ - \text{CH}_3\text{OH}$, 16), 336 ($\text{M}^+ - \text{CH}_3\text{OH} - \text{COC}_6\text{H}_5$, 2), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_6$: C, 71.03; H, 5.70; N, 2.95. Found: C, 71.42; H, 5.46; N, 2.84.

II.4.10 Photolysis of a Mixture of cis-1-Cyclohexyl-2,3-dibenzoylaziridine (21b) and Dimethyl Acetylenedicarboxylate (DMAD). A mixture of 21b (1.0 g, 3.0 mmol) and DMAD (0.85 g, 6.0 mmol) in acetonitrile (350 mL) was irradiated (Hanovia 450 W, medium pressure Hg lamp) for 1 h at ca. 15-20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave excess DMAD (0.36 g), bp 95-98 °C (19 mm). Further elution with a mixture (1:1) of benzene and petroleum ether gave 90 mg (8%) of unidentified compound ($\text{C}_{20}\text{H}_{18}\text{O}_6$), mp 189-190 °C (mixture mp), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Continued elution with

a mixture (1:1) of benzene and petroleum ether gave 50 mg (3%) of the pyrrole 63, mp 109-110 °C (mixture mp), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Further elution with benzene gave 770 mg (54%) of the 3-pyrroline 61, (superimposable ir spectrum). Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 100 mg (9%), of unidentified compound ($C_{21}H_{23}NO_5$), mp 153-154 °C (mixture mp), after recrystallization from a mixture (3:7) of benzene and petroleum ether.

II.4.11 Laser Flash Photolysis.²¹ For laser flash photolysis, pulse excitation was carried out mostly at 337.1 nm (2-3 mJ, ~8 ns), employing a Molelectron UV-400 nitrogen laser system. For some experiments, the output (third harmonic, 355 nm, 5-20 mJ, 6 ns) from a Quanta-Ray Nd-YAG system was also used. The transient phenomena were observed in terms of absorption in 2-3 mm quartz cells by using a kinetic spectrophotometer described elsewhere.^{31,61} Unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon or nitrogen. In the experiments requiring a large number of laser shots (e.g., for wavelength-by-wavelength measurements of transient absorption spectra), a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell.

II.4.12 Pulse Radiolysis.²¹ For pulse radiolysis, 5 ns electron pulses from the Notre Dame 7-MeV ARCO LP-7 linear

accelerator was used at dose rates of 2×10^{16} eV/g per pulse. The details of computer-controlled spectrophotometric detection system are available elsewhere.^{62,63} Nitrogen-saturated benzene solutions were allowed to flow through a quartz cell (1 cm path length), that was irradiated with electron pulses in a right-angle geometry with respect to the analyzing light. The conventional lamp flash photolysis system is described elsewhere.⁶⁴

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CHAPTER III

PHOTOTRANSFORMATIONS OF BENZOPYRANOLS

III.1 ABSTRACT

The phototransformations of several 4H-benzopyran-4-ol systems incorporating the 1,2-dibenzoylalkene moiety such as 2,3-dibenzoyl-4H-1-benzopyran-4-ol (16a), 2,3-dibenzoyl-4-methyl-4H-1-benzopyran-4-ol (16b), and 2,3-dibenzoyl-1H-naphtho[2,1-b]pyran-1-ol (16c) have been examined by steady-state photolysis, product analysis and nanosecond laser flash photolysis. These benzopyranols 16a-c, themselves, were prepared by the nucleophilic addition of the corresponding *o*-hydroxy carbonyl compounds 12a-c to dibenzoylacetylene (DBA, 13).

Direct photolysis of 16a-c gave the corresponding 2H-1-benzopyran-2-ols 15a,c and/or their methoxy analogues 18a,c or the anhydro derivative 19b, presumably through the intermediacy of the carbocations 21a-c, generated as a result of photodehydroxylation. No product such as butenoic acid/ester derivatives, attributable to the intramolecular phenyl group migration along the 1,2-dibenzoylalkene moieties could be observed.

The laser flash photolysis of the 4H-benzopyranols 16a-c and the 2H-benzopyranols 15a,c showed the formation of their triplets, characterized by unusually short lifetimes (submicrosecond), indicating the reactive nature of the triplets. In addition, in the case of 15a,c, longer-lived transient species,

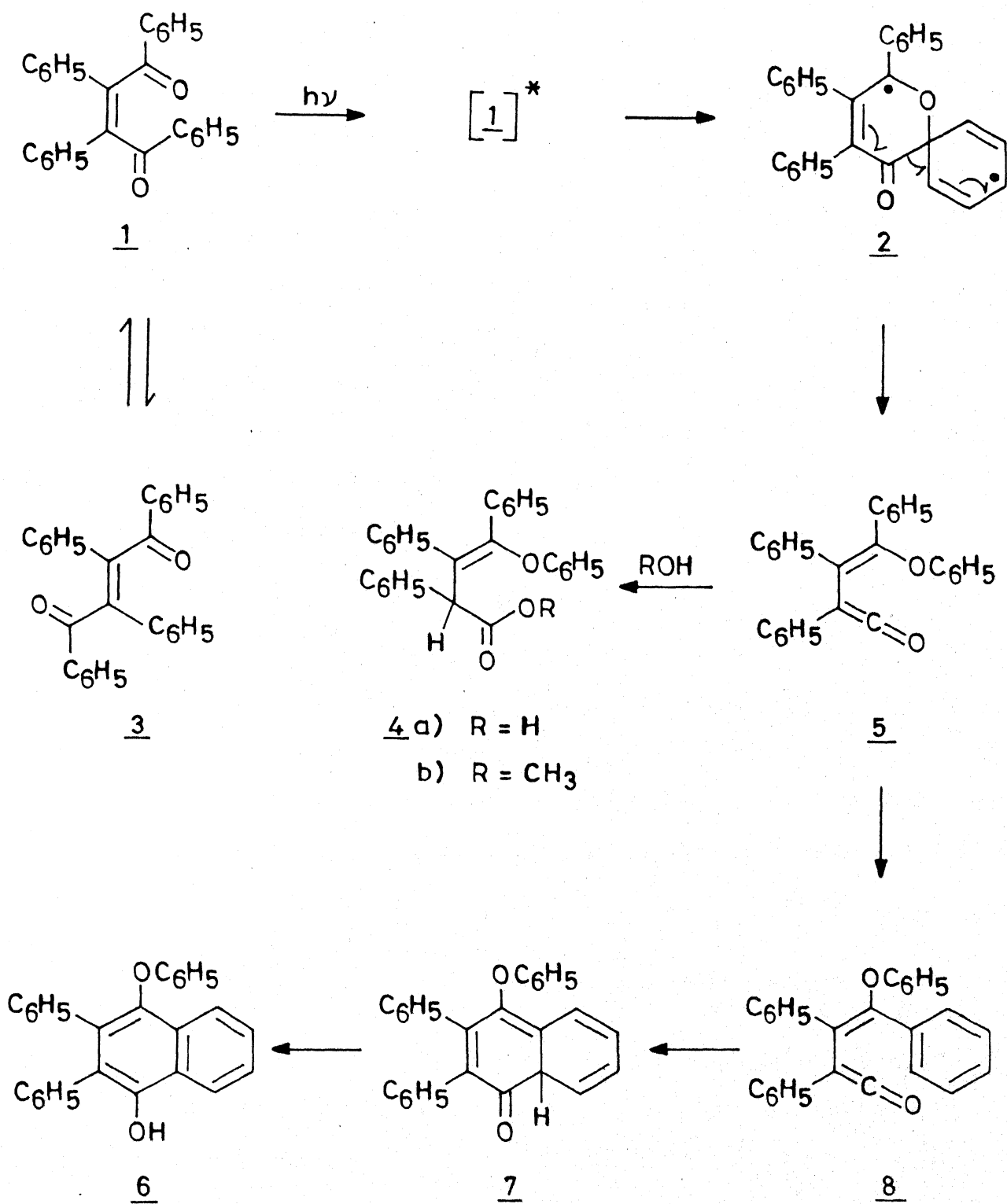
characterized by absorptions at long wavelengths (700-800 nm) were observed; these were best assigned as the biradicals produced as a result of ring-opening via triplet-mediated C₂-O bond cleavage.

III.2 INTRODUCTION

1,2-Dibenzoylalkenes are known to undergo interesting photorearrangements leading to ketene-derived products, besides cis-trans isomerization.¹⁻⁵ Thus, it has been reported that the irradiation of cis-dibenzoylstilbene (1) in a mixture (1:1) of benzene and methanol, for example, gives a mixture of methyl 4-phenoxy-3,4,5-triphenyl-3-butenate (4b) and trans-dibenzoylstilbene (3).⁴ Similar transformations have been observed in the case of dibenzoylstyrene, 1,2-dibenzoylethylene and related dibenzoylalkenes. Padwa et al.³ have shown that the photolysis of trans-dibenzoylstilbene (3) gives rise to different products, depending on the solvent employed. Thus, the photolysis of 3 in dry benzene, for example, gave a mixture of cis-dibenzoylstilbene (1) and 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (6), whereas 4-phenoxy-2,3,4-triphenyl-3-butenic acid (4a) was formed in aqueous dioxane. The formation of the different products in such reactions has been rationalised in terms of the pathways shown in Scheme III.1.^{3,4}

Recent studies from this laboratory have shown that the irradiation of cis-1,2-dibenzoylalkenes, wherein the cis-trans isomerization is restricted due to structural constraints, gives

Scheme III.1



rise to the ketene-derived products predominantly.⁶ Also, it has been shown that the phototransformations of 1,2-dibenzoylalkenes are strongly influenced by the nature of the substituents present in them.⁷⁻¹⁹ Thus, dibenzobarrelenes containing 1,2-dibenzoylalkene moieties have been found to undergo reactions characteristic of the barrelene chromophore,^{9-12,19} whereas 1-imidazolyl and 1-pyrazolyl-1,2-dibenzoylalkenes undergo the dibenzoylalkene rearrangement, as well as electrocyclic reactions involving aryl substituents present on the imidazolyl and pyrazolyl rings.¹³⁻¹⁶ In contrast to these, 1-aziridinyl-1,2-dibenzoylethylenes have been found to undergo facile ring-expansion reactions leading to pyrazoline derivatives and photofragmentation reactions.^{16,17}

In the present studies, we have examined the phototransformations of some representative 4H-1-benzopyran-4-ols incorporating the 1,2-dibenzoylalkene moiety with a view to studying the nature of products formed in these cases and also the reaction pathways. The photoreactions of these systems can, in principle, follow two distinct pathways - one involving the reaction of the 1,2-dibenzoylalkene moiety and the other involving the benzopyranol fragment. The anticipation for the latter reaction pathway has been based on some of the recently reported examples of adiabatic photodehydroxylation reactions of related systems. Thus, the photodehydroxylation of 9-phenylxanthen-9-ol (9) to give the carbocation 10,

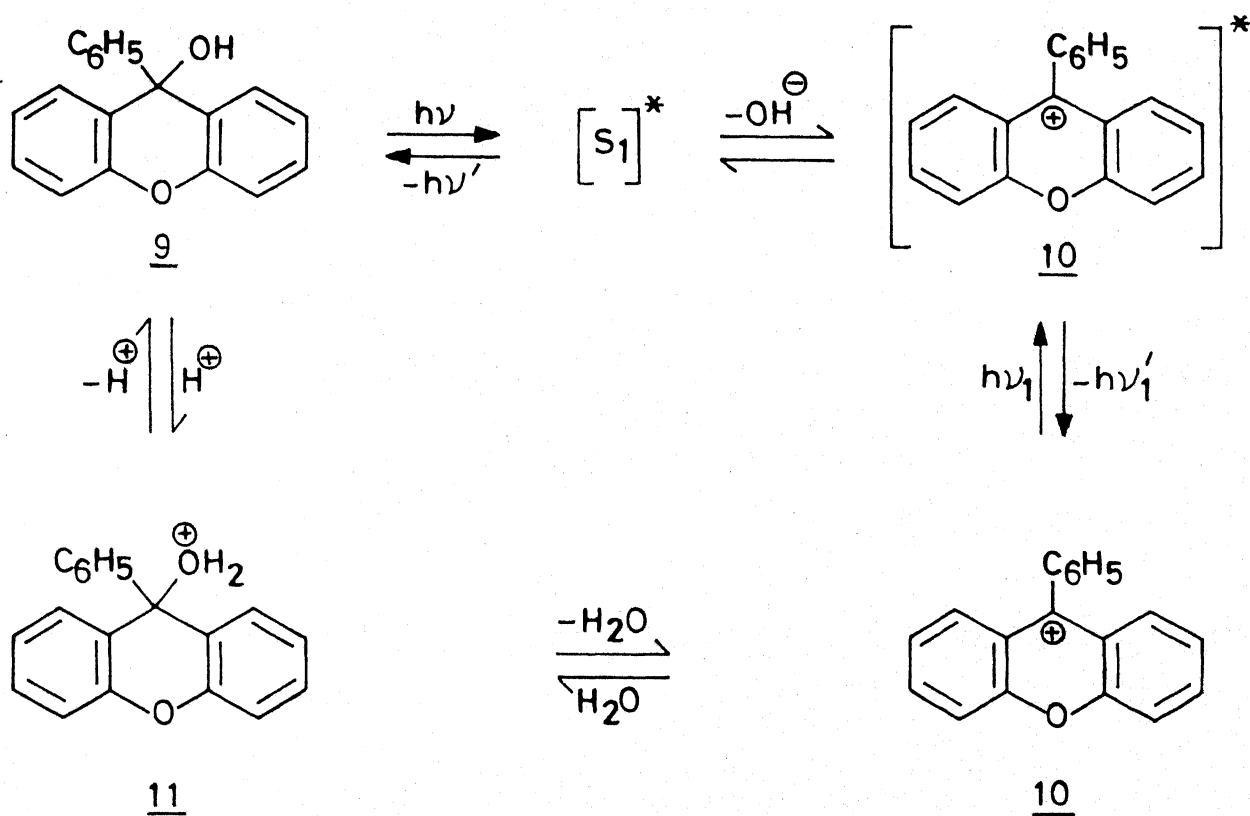
has been suggested to proceed through its singlet excited state by an adiabatic process. The same carbocation 10 is formed when 9 is treated with a strong acid, which could be independently excited to its singlet excited state, 10^{*} (Scheme III.2).²⁰

The 4H-1-benzopyran-4-ols that we have taken up for steady-state photolysis studies include 2,3-dibenzoyl-4H-1-benzopyran-4-ol (16a), 2,3-dibenzoyl-4-methyl-4H-1-benzopyran-4-ol (16b), and 2,3-dibenzoyl-1H-naphtho[2.1-b]pyran-1-ol (16c). The steady-state photolysis studies of a few other related systems such as 2,3-dibenzoyl-2H-1-benzopyran-2-ol (15a), 2,3-dibenzoyl-4-methylene-4H-1-benzopyran (19b), and 2,3-dibenzoyl-4H-1-benzopyran-4-one (20a) have also been attempted. In addition to 16a-c and 15a, 2,3-dibenzoyl-3H-naphtho[2,1-b]pyran-3-ol (15c), 2,3-dibenzoyl-2-methoxy-2H-1-benzopyran (18a), and 2,3-dibenzoyl-3-methoxy-3H-naphtho[2,1-b]pyran (18c) were also subjected to nanosecond laser flash photolysis studies to characterize the nature of the transients involved in their phototransformations.

III.3 RESULTS AND DISCUSSION

III.3.1 Preparation of Starting Materials. Addition of several ortho-disubstituted nucleophiles to acetylenic ketones has been successfully employed in the synthesis of a variety of heterocycles.²¹⁻²³ It has been reported earlier from this laboratory that the nucleophilic addition of o-hydroxy carbonyl compounds such as 12a,b to dibenzoylacetylene (DBA, 13) gives

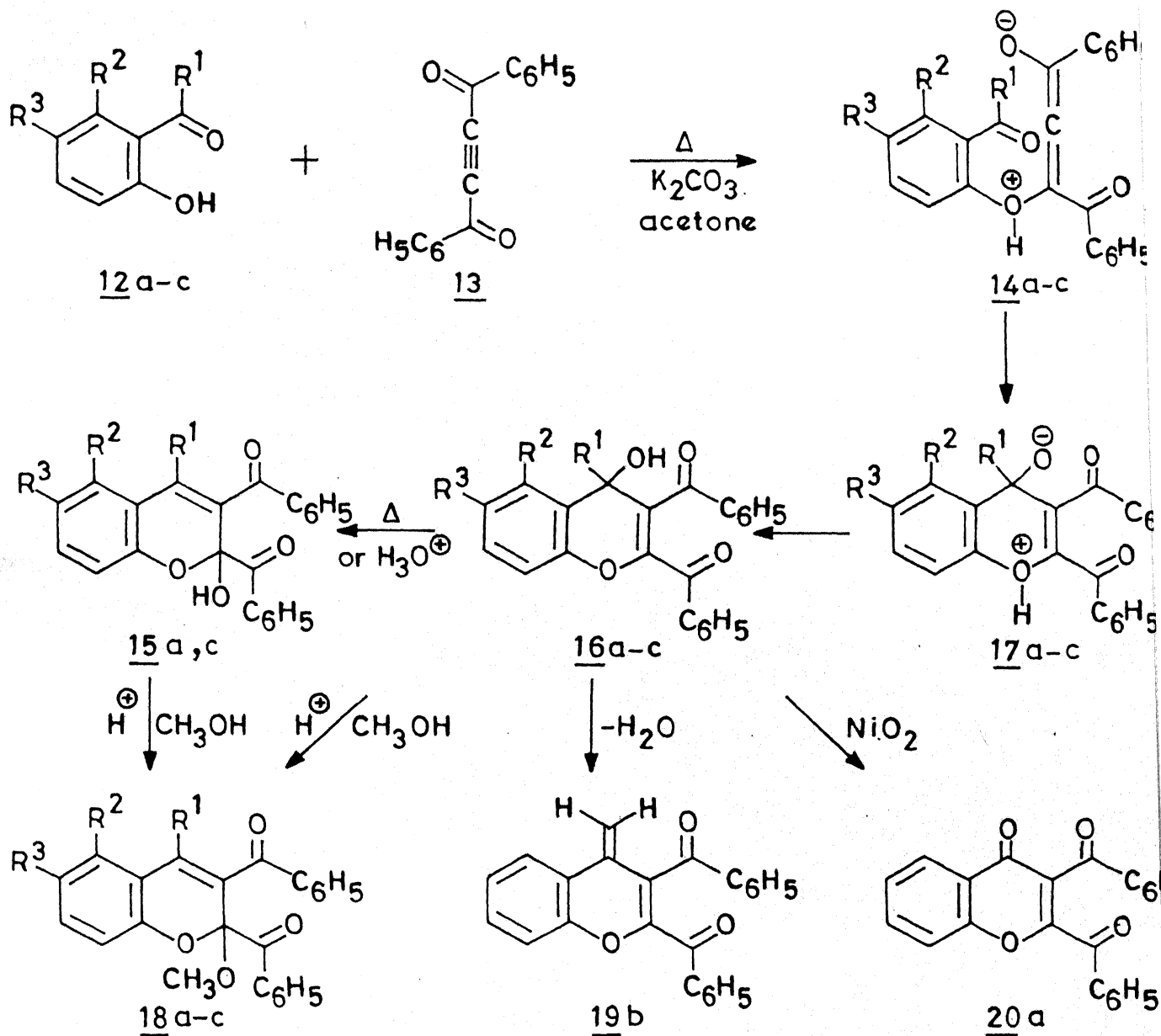
Scheme III.2



rise to the corresponding 4H-1-benzopyran-4-ols 16a,b or the 2H-1-benzopyran-2-ol 15a, depending on the reaction conditions.³⁴ In the present studies, we have prepared, 2,3-dibenzoyl-1H-naphtho[2,1-b]pyran-1-ol (16c, 86%) by the addition of 2-hydroxy-1-naphthaldehyde (12c) to DBA (13) in the presence of anhydrous potassium carbonate in acetone at room temperature. The 3H-naphtho[2,1-b]pyran-3-ol 15c (52%) was prepared by the acid-catalysed isomerization of 16c. The benzopyranone 20a was prepared through the nickel peroxide oxidation of 16a (96%) in benzene at 25 °C, whereas the 4-methylene-4H-1-benzopyran 19b was prepared through the acid-catalysed dehydration of 16b (Scheme III.3). The structures of 15c, 16c, 19b, and 20a were established on the basis of analytical results, spectral data and chemical transformations.


III.3.2 Preparative Photochemistry and Product Identification. Irradiation (RPR 3000 Å) of 16a in benzene and in acetone gave 15a exclusively in 65% and 74% yields, respectively, whereas that of 16a in methanol gave a mixture of 15a (58%) and 18a (17%) (Scheme III.4). The photolysis of 16b in benzene, acetone and in methanol, on the other hand, gave the dehydration product, 2,3-dibenzoyl-4-methylene-4H-1-benzopyran (19b) in good yields (55-63%), as the only isolable product. Irradiation of 16c in benzene gave a mixture of 15c (44%) and (E)-1-(1-formyl-2-naphthoxy)-1,2-dibenzoylethylene (22c, 2%), whereas the irradiation in acetone gave 15c (85%), as the only isolable product. In contrast, the photolysis of 16c in methanol

Scheme III.3

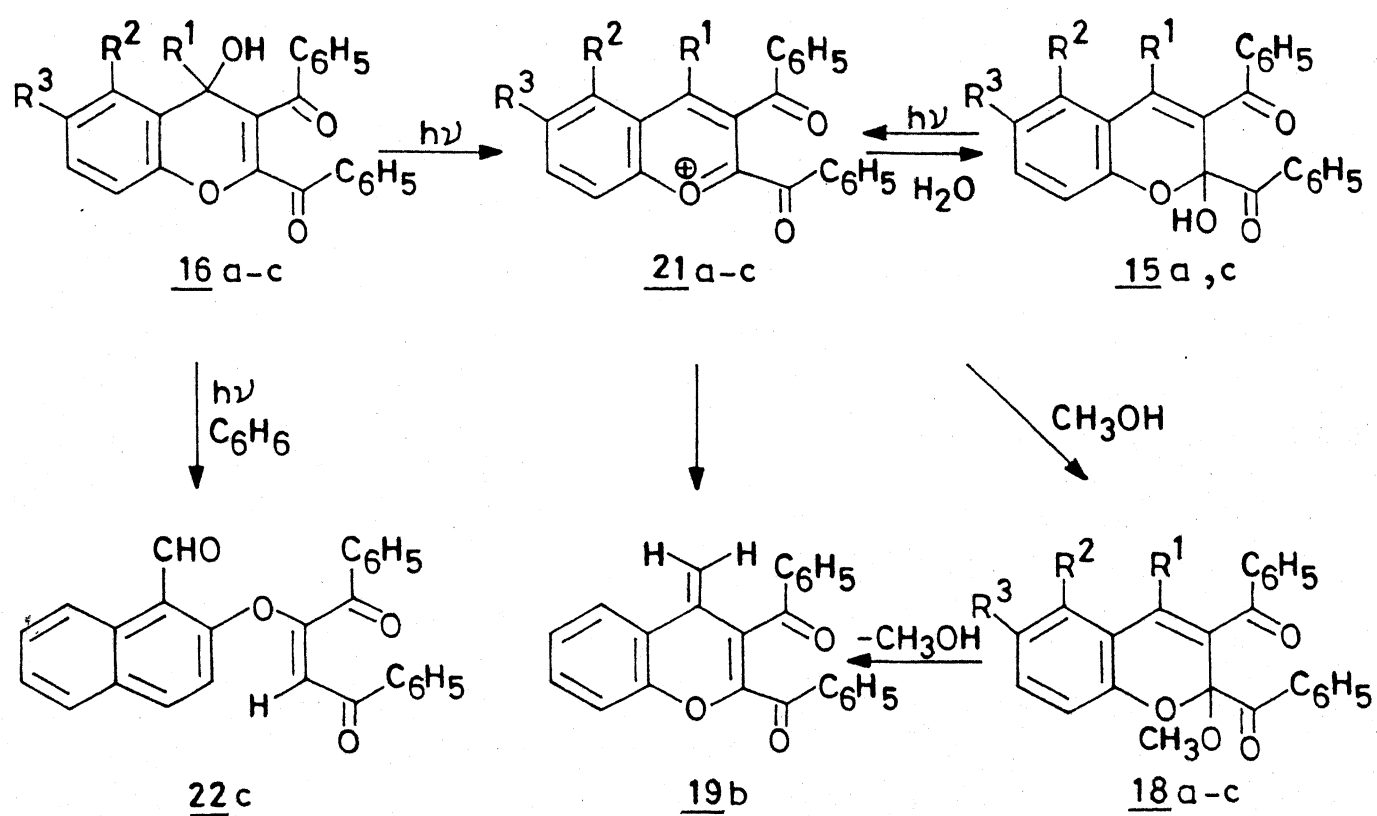


a) $R^1 = R^2 = R^3 = H$

b) $R^1 = CH_3$; $R^2 = R^3 = H$


c) $R^1 = H$; $R^2, R^3 =$ 

Scheme III.4



a) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$

b) $\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{R}^3 = \text{H}$

c) $\text{R}^1 = \text{H}$; $\text{R}^2, \text{R}^3 =$ 

gave a mixture of 15c (40%) and 2,3-dibenzoyl-3-methoxy-3H-naphtho[2,1-b]pyran (18c, 17%) (Scheme III.4).

Irradiation of a representative 2H-1-benzopyran-2-ol such as 15a in methanol gave the methoxy derivative 18a (36%), along with a 30% recovery of the unchanged starting material (15a) (Scheme III.4). Attempted irradiation of 2,3-dibenzoyl-4-methylene-4H-1-benzopyran (19b) and 2,3-dibenzoyl-4H-1-benzopyran-4-one (20a) in different solvents did not give any isolable product, most of the 19b and 20a (60-84%) could be recovered unchanged, in each case.

The structures of all the photoproducts were established on the basis of analytical results, spectral data and chemical evidence, wherever possible. Thus, the treatment of the 4H-1-benzopyran-4-ols 16a,c with hydrochloric acid in methanol under reflux, gave the corresponding 2H-1-benzopyran-2-ols 15a,c in 44% and 52% yields, respectively. Treatment of 16a,c with *p*-toluenesulphonic acid in dry methanol at 15-20 °C, on the other hand, gave the methoxy derivatives 18a,c (44-57%). The stereochemistry across the alkene bond in 22c has been assigned as that of the *E*-configuration, on the basis of steric considerations and literature precedents.³⁵

The formation of the different products in the steady-state irradiation of the benzopyranols 15a and 16a-c can be understood in terms of the pathways shown in Scheme III.4. Photodehydroxylation from the excited state(s) of 15a, 16a-c

gives the carbocations 21a-c, which undergo subsequent transformations to the observed products, depending on the reaction conditions. Thus, the reaction of 21a,c with adventitious water will give rise to the 2H-1-benzopyran-2-ols 15a,c, whereas the reaction of 21a,c with methanol will lead to the corresponding methoxy derivatives 18a,c. The preferential formation of the 2H-1-benzopyran-2-ols 15a,c or the methoxy analogues 18a,c from 21a,c may be attributed to their thermodynamic stability over the corresponding 4H-pyran analogues. These observations are in agreement with earlier reports on the kinetic and thermodynamic control over the reaction of methoxide anion with several pyrilium cations and related systems.³⁶⁻³⁸

The formation of 19b from 16b can also be explained in terms of the carbocation intermediate 21b, which can undergo ready deprotonation under the reaction conditions. The intermediacy of 21b in the phototransformation of 16b was confirmed through ¹H NMR evidence. Thus, when a solution of 16b in benzene, after 20 min of irradiation, was treated with methanol and the solvent removed under vacuum, an initial mixture of the methoxy derivative 18b and the dehydration product 19b in a 1:3 ratio was present, as evidenced by ¹H NMR signals. Subsequent workup, however, resulted in the isolation of 19b, as the only product. The methoxy derivative 18b, formed initially may be getting transformed to 19b, under the conditions of workup.

It is pertinent to note that in the course of the irradiation of the benzopyranols 16a-c, none of the products resulting from the 1,2-dibenzoylalkene rearrangement¹⁻⁵ could be observed. It appears that the most facile process from the excited states of these substrates is the photodehydroxylation reaction, as against the potential 1,2-dibenzoylalkene rearrangement.

III.3.3 Laser Flash Photolysis Studies.³⁹ In order to shed light on the probable intermediates involved in the observed phototransformations, the 4H-benzopyranols 16a-c, and some of the photoproducts derived thereof, such as 15a,c and 18a,c, were subjected to nanosecond laser flash photolysis studies in benzene and methanol solutions at room temperature (295 K). Because of strong ground-state absorptions of these compounds at 337.1 nm, it was convenient to employ, for direct excitation, N₂ laser pulses (2-3 mJ, 8 ns) from a Molelectron UV-400 source. In all of our experiments, the concentration of the solutions were ≤ 5 mM (absorbance = 0.2-1.0 in 2 mm cells at 337.1 nm).

Upon 337.1 nm laser pulse excitation, benzene and methanol solutions of 16a-c produce short-lived species, characterized by submicrosecond lifetimes ($\tau = 0.2-0.3$ μ s) and broad absorption spectra ($\lambda_{\text{max}} = 370-375$ nm). The transient absorption spectra and decay traces in benzene are presented in Figure III.1. The long-lived residual absorptions at the end of the decay of the short-lived components (Figure III.1) are very weak. Based

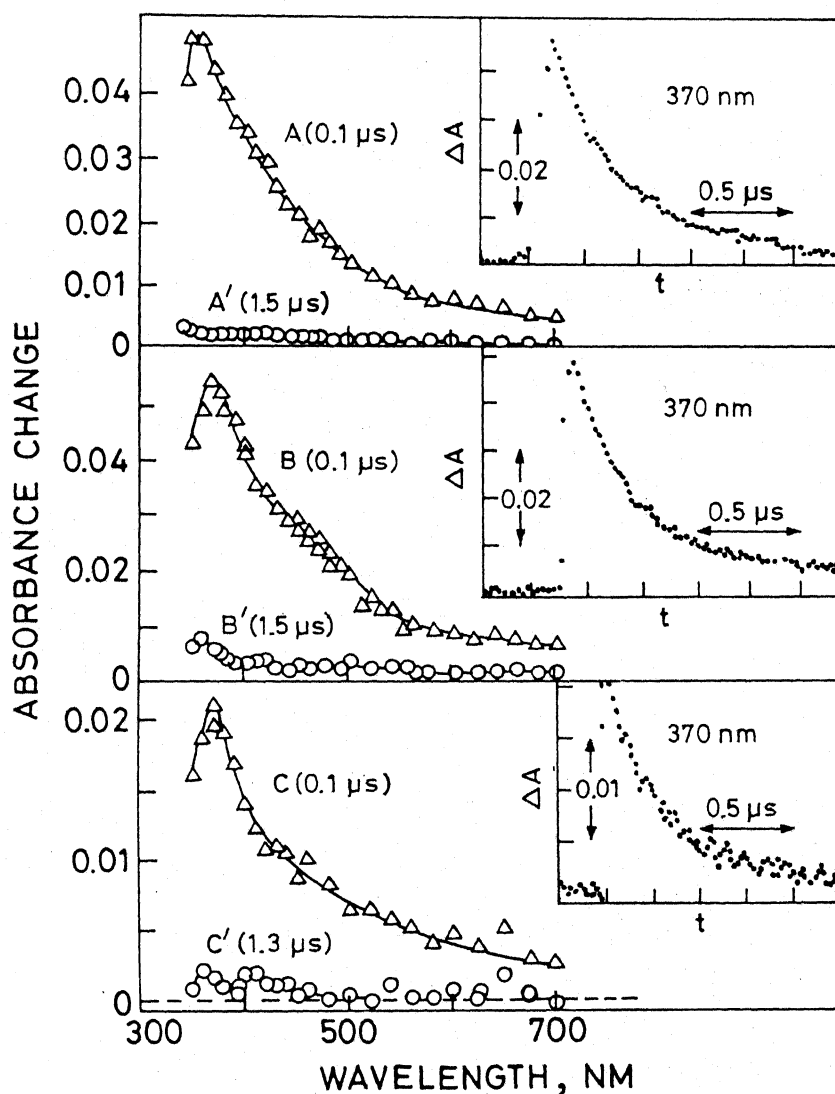


Fig. III.1 Transient absorption spectra from 337.1 nm laser pulse excitation of (A, A') 16a, (B, B') 16b and (C, C') 16c in benzene at 295K. Insets: kinetic traces at 370nm in respective cases. The times (after laser flash) at which the spectra were observed are given in the figures.

on the following evidence, the short-lived components have been assigned to the triplets of the substrates 16a-c. First, the transients were readily quenched by oxygen, nitroxyl radical (4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl, HTEMPO) and ferrocene, the rate constants for quenching by ferrocene being in the limit of diffusion control ($k_q = 5.3-5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene). Second, when benzene solutions of 16a-c containing 0.1-0.5 mM β -carotene were flash-photolysed at 337.1 nm, growths of transient absorptions at 520-600 nm due to β -carotene triplet were observed, suggesting that triplets acting as excitation donors to β -carotene were formed. The kinetics of the formation of β -carotene triplet absorption were faster than, but close to, those of the decay of the 360-370 nm transients from 16a-c. Although in these experiments β -carotene absorbed a substantial fraction of the laser photons (up to 70%), there was practically no triplet formation as a result of the direct excitation because of its negligible intersystem crossing efficiency (this was confirmed by blank experiments in which β -carotene solutions were flash photolysed in the absence of donors). Third, the laser pulse excitation (337.1 nm) of benzophenone (BP) in benzene in the presence of 0.4-2.0 mM 16a-c showed the enhancement of the decay of BP triplet (monitored at 532 nm); the bimolecular rate constant for BP triplet quenching by 16a-c were estimated in the range $(3-4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. At relatively high concentrations (1.5-2.0 mM) of 16a-c, the delayed formation of their short-lived triplets was clearly indicated at 360-450 nm as a result of energy transfer from BP

triplet. In these experiments, the ground-state absorbance due to BP at the laser excitation wavelength was relatively high (2.0-3.0 in 2 mm cells at 337.1 nm) so that only $\leq 20\%$ of the laser photons were absorbed by the substrates (acceptors). None of the compounds 16a-c proved to be an efficient quencher for camphorquinone (CQ) triplet, as established by experiments in which the latter was produced in benzene under 485 nm laser pulse excitation of CQ in the presence of 16a-c. The decay kinetics of CQ triplet in the presence (5 mM) and in the absence of 16a-c was found to be practically identical. This suggests that the triplet energies (E_T) of 16a-c are higher than that of CQ ($E_T = 52 \text{ kcal mol}^{-1}$).⁴⁰

Unfortunately, the long-lived residual absorptions following the decay of the triplets in the case of 16a-c were not strong. This precluded any meaningful experiments to identify them as carbocations 21a-c. Therefore, we explored the possibility of photogenerating the carbocations from the 2-pyrans 15a,c and their methoxy analogues 18a,c. In particular 15a was investigated in detail by laser flash photolysis.

Upon 337.1 nm laser pulse excitation, benzene and methanol solutions of 15a produced a long-lived transient species, characterized by a broad absorption band system at long wavelengths, i.e., 600-800 nm (in addition to sharper and stronger absorptions at 340-370 nm) (Figure III.2). As shown in the insets of Figure III.2, the transient decayed over microseconds with

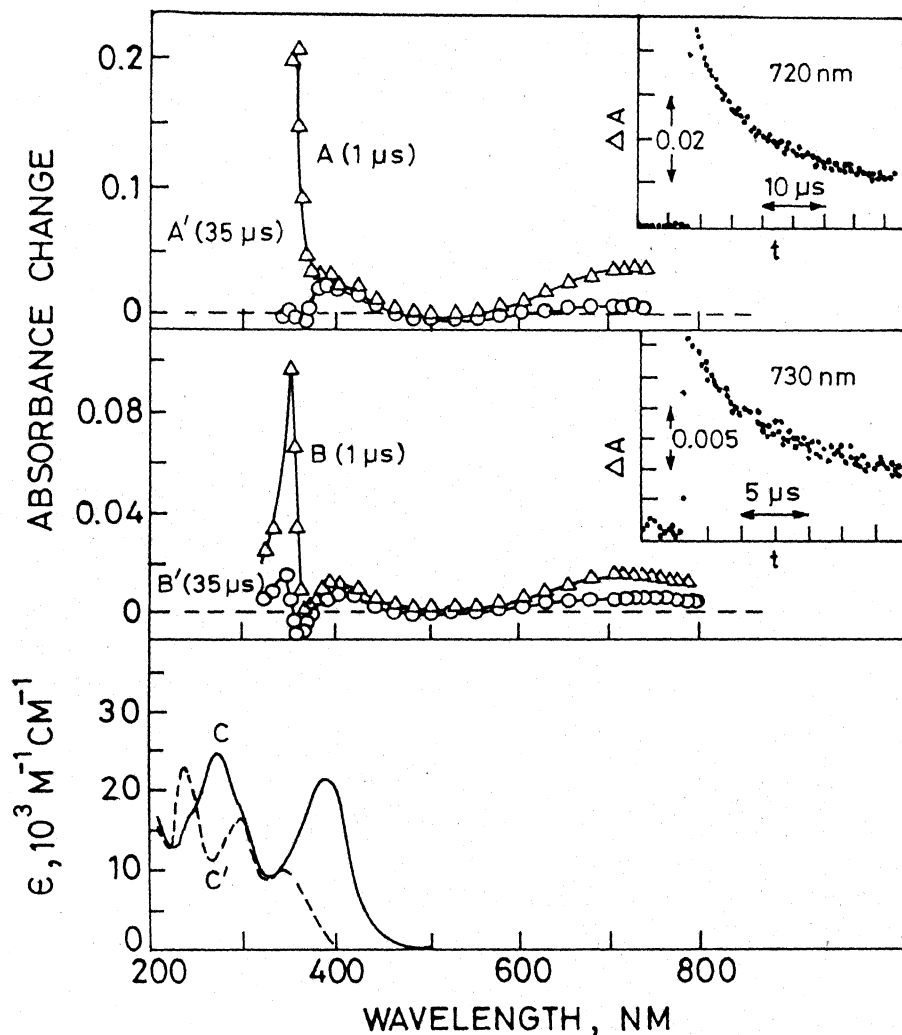


Fig. III.2 Transient absorption spectra from 337.1 nm laser pulse excitation of 15a in (A, A') benzene and (B, B') methanol at 295 K. The curves C and C' represent the absorption spectra of the carbocation from 15a in 10 M H_2SO_4 (see text) and that of 15a, respectively. Insets: typical kinetic traces at long wavelength in benzene and methanol in respective cases.

complex kinetics. In the presence of oxygen, the decay kinetics in methanol became predominantly first-order, the observed lifetime being 0.55 μs in air-saturated methanol. Based on this lifetime, the rate constant for oxygen quenching was estimated to be $9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ in methanol. In air-saturated benzene also, the decay of the 750 nm species became considerably enhanced, although this could not be fitted well into single-exponential first-order kinetics. Another interesting property of the 750 nm species was that it was quenched by the nitroxyl radical, HTEMPO, the rate constant for the quenching being $1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (in benzene). On the other hand, the decay behaviour of the 750 nm species in benzene remained practically unchanged upon addition of ferrocene (up to 6.1 mM), suggesting that it cannot possibly be a triplet with $E_T > 40 \text{ kcal mol}^{-1}$.

In order to know if the oxygen quenching of the 750 nm species leads to the formation of singlet oxygen ($^1\text{O}_2^*$, $^1\Delta_g$), experiments were carried out in which air-saturated solutions of 15a in benzene and methanol and that of BP in benzene, optically matched at 337.1 nm (absorbance = 2.0 in 2 mm cells), were flash photolyzed at this wavelength in the presence of 0.05 mM diphenylisobenzofuran (DPBF). The bleaching of DPBF as a result of its reaction with $^1\text{O}_2^*$ (endo-peroxide formation) was monitored at 420 nm (over $\sim 100 \mu\text{s}$). Interestingly, the relative amounts of photogenerated $^1\text{O}_2^*$, measured in terms of negative absorbance change due to DPBF depletion, was about twice as much in the case of 15a as in the case of BP. Since the triplet of 15a is

too short-lived to be significantly quenched by oxygen in air-saturated solutions (see later), the oxygen quenching of the 750 nm species appears to be the most reasonable source of $^1\text{O}_2^*$ in the case of 15a. It should be noted that the bleaching of DPBF in the case of 15a was not observed in deoxygenated solutions.

The transient behaviour of the 750 nm species in mildly acidic and basic conditions was studied using solutions of 15a in a mixture (1:1) of methanol and water (v/v). Addition of sulphuric acid up to 2.0 mM did not affect the decay kinetics of the observed transient species. However, upon gradual addition of NaOH (up to 1.2 mM), the transient absorption at 340-350 nm was seen to undergo progressively enhanced decay. Concomitant to this decay, there was growth of transient absorption at 360-380 nm. From the linear dependence of the pseudo-first-order rate constant for transient absorption decay at 340 nm on [NaOH], the rate constant for the reaction of the 340 nm transient with the base was measured to be $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (in a mixture (1:1) of methanol and water, v/v). It should be noted that the ground state spectrum of 15a in aqueous methanol does not change in the presence of low concentration of sulphuric acid employed, indicating the lack of formation of the carbocation 21a, under this condition. The carbocation 21a is apparently formed (as shown by the development of yellow colouration) when the substrate was added, as a small quantity of solid or acetonitrile solution, to strong sulphuric acid (10 M). The

resultant absorption spectrum is shown in Figure III.2, part C; the extinction coefficient in this figure was calculated on the basis of the assumption that the amount of 15a added to the acid is completely dehydroxylated to the carbocation 21a and that there is no loss of 15a via side or subsequent reactions. In the weakly alkaline medium, i.e., in the presence of sodium hydroxide (1.2 mM) in aqueous methanol, 15a developed a long tail (370-550 nm) beyond its lowest-energy absorption band system ($\lambda_{\text{max}} = 345 \text{ nm}$); the intensity of this tail absorption slowly increased with time (over hours) as the basic solution was allowed to stand in the dark, suggesting that it was due to the product of a thermal reaction of 15a with the base (most probably, base-catalysed ring-opening to give the corresponding phenoxide derivative).³⁴ The laser flash photolysis experiments in the basic medium (described above) were carried out within minutes after the addition of sodium hydroxide, to ensure that the light absorption at excitation wavelength (337.1 nm) was still dominated by the unchanged substrate (15a).

The monitoring of transient absorption on a short time domain (50-100 ns) following the laser pulse excitation of 15a in benzene or methanol shows an extremely short-lived species that absorbs at 400-500 nm ($\lambda_{\text{max}} \sim 440 \text{ nm}$). In benzene the decay ($\tau \leq 10 \text{ ns}$) of this species nearly follows the laser pulse; the decay lifetime is shown to be longer ($\sim 20 \text{ ns}$) in methanol. Because of the short lifetime, no quenching studies could be convincingly done to establish the identity of the

transient. However, based on the observation of an analogous but longer-lived phototransient that is characterized as the triplet of the methoxy derivative 18a (see later), it seems extremely likely that the 10-20 ns transient observed in the case of 15a constitutes its triplets.

The transient phenomena observed upon 337.1 nm laser flash photolysis of 15c in benzene and methanol were dominated by fast-decaying species ($\tau \sim 0.4 \mu\text{s}$) having an absorption maximum at 540 nm; this was followed by a longer-lived component ($\tau \sim 85 \mu\text{s}$ in benzene), the absorption of which extended to long wavelengths (λ_{max} 's = 415-420 and $\sim 750 \text{ nm}$) (Figure III.3). Detailed quenching studies on the short-lived component ($\lambda_{\text{max}} = 540 \text{ nm}$) using oxygen, HTEMPO and ferrocene establish this to be due to the triplet of 15c; these kinetic studies also showed that the longer-lived component was a product of the decay of this triplet (that is, the magnitude of the residual absorption decreased proportionately as the triplet is progressively quenched by ferrocene or HTEMPO). The longer-lived component, monitored at 415-420 nm, was also quenched by oxygen and HTEMPO with rate constants of 1.2×10^8 and $1.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, respectively (in benzene). This behaviour is reminiscent of that observed for the 750 nm species in the case of 15a (vide supra).

Experiments on the methoxy derivatives 18a,c, similar to those described above for 15a,c, led to the characterization of their triplets ($\lambda_{\text{max}}^{\text{T}} = 460 \text{ nm}$ for 18a and 550 nm for 18c, see Figure III.4, parts A and B). Note that the triplets of the

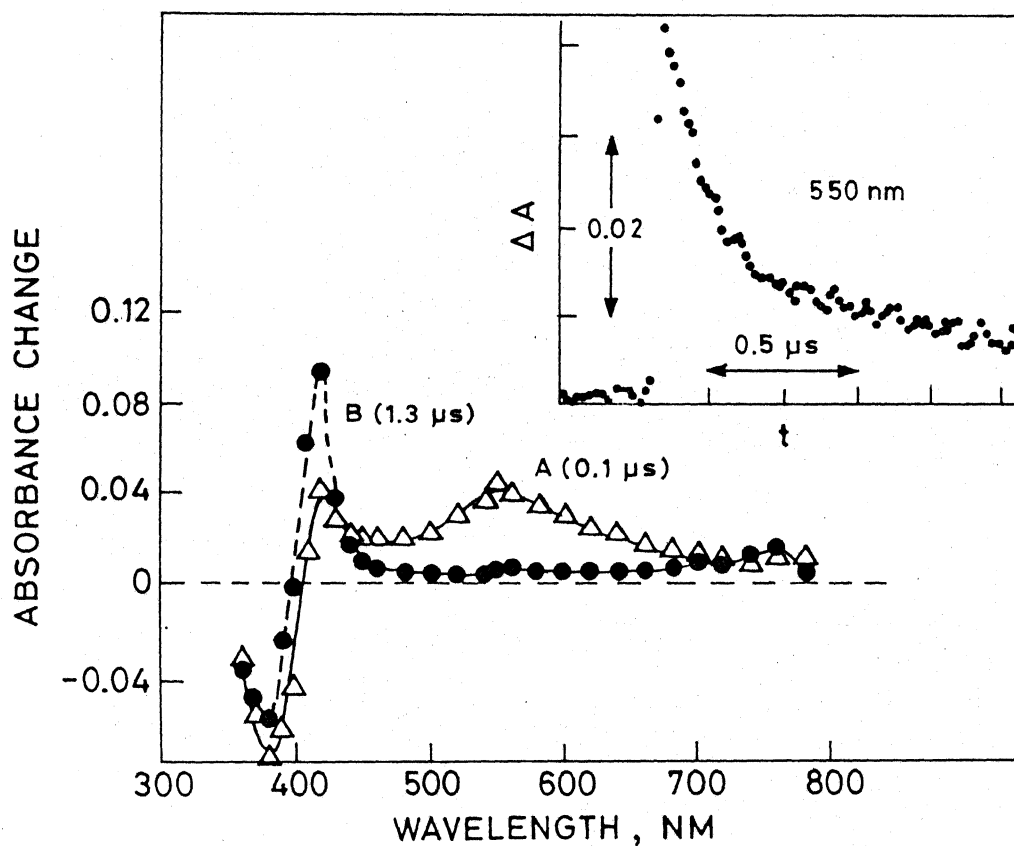


Fig. III.3 Transient absorption spectra observed at (A) 0.1 and (B) 1.3 μs , following 337.1 nm laser flash excitation of 15c in benzene at 295 K. Inset: kinetic trace for transient absorption decay at 550 nm.

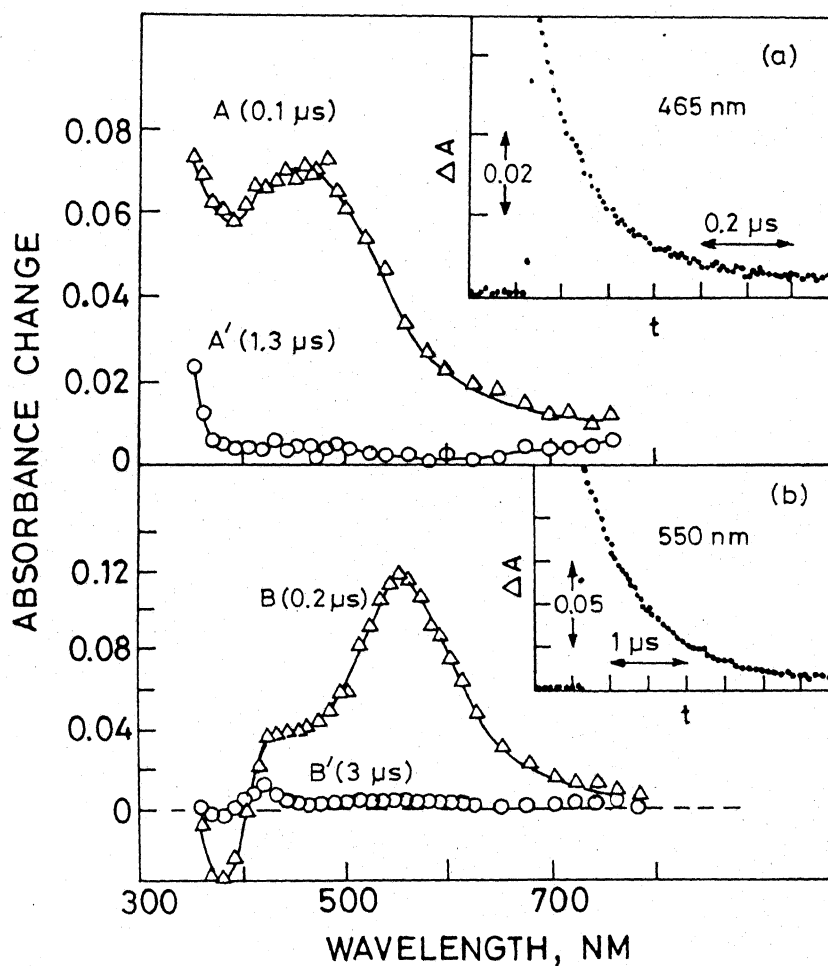


Fig. III.4 Transient absorption spectra from 337.1 nm laser flash excitation of (A, A') 18a and (B, B') 18c in benzene at 295 K. The times (after laser pulse) at which the spectra were observed are given in the figures. Insets: kinetic traces from triplet absorption decay of (a) 18a and (b) 18c in benzene.

methoxy derivatives (18a,c) were significantly longer-lived than their hydroxy analogues (15a,c). Triplet mediated, longer-lived residual absorptions, spectrally similar to those observed in the case of 15a,c, but considerably weaker in intensity, were also observed in the case of 18a,c (Figure III.4, parts A' and B'). The spectral and kinetic data for the triplets of the various substrates are summarized in Table III.1.

The short lifetimes (submicrosecond) of the benzopyranol triplets reflect their reactive nature. Although each of these molecules has a double bond as a part of the chromophore, twisting about this bond in the triplet state should not be facile because of the constraint imposed by the ring. Also, such a relaxation in the triplet state (if extensive would manifest itself in the rate constants for quenching by oxygen and ferrocene (that is, k_q^T by oxygen would be relatively high while k_q^T by ferrocene would be relatively low). In view of the photochemistry observed under steady state irradiation (described earlier), dehydroxylation to the carbocations 21a-c appears to be a major photochemical pathway for the decay of the triplets of 15a,c and 16a-c.

One can think of several possible assignments for the long-lived species (600-800 nm) observed in the case of 15a,c and 18a,c. As shown below, these include: (i) carbocations 21a,c in the ground state, (ii) triplet states of carbocations 21a,c produced adiabatically on the triplet surfaces of 15a,c or 18a,c, (iii) radicals produced as a result of homolytic scission of the hydroxyl or methoxy group and (iv) ring opened biradicals from

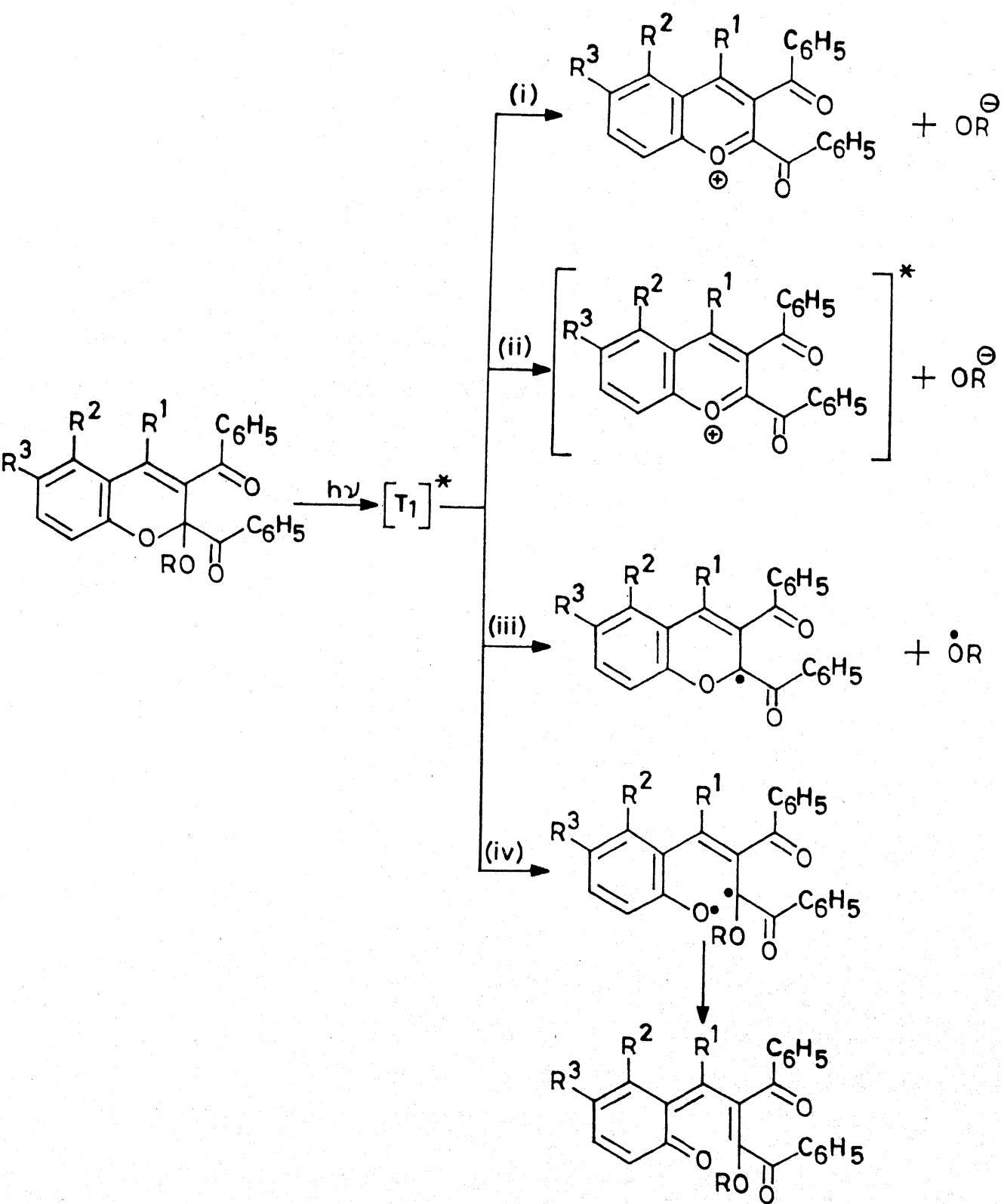
TABLE III.1 Absorption-spectral and Kinetic Properties of Triplets in Benzene at 295 K

sub- strate	λ_{\max}^T , nm ^a	τ^T , μs ^b	k_q^T , $10^9 \text{ M}^{-1}\text{s}^{-1}$ ^c		
			O ₂	HTEMPO	ferrocene
<u>16a</u>	365	0.33 (0.17)	1.2	1.1	5.9
<u>16b</u>	370	0.27 (0.24)	1.1	0.74	5.3
<u>16c</u>	370	0.28 (0.30)	0.97	0.95	5.3
<u>15a</u>	~440	≤ 0.01 (~0.02)			
<u>15c</u>	460	0.12 (0.15)	1.3	0.54	6.2
<u>18a</u>	540	0.35 (0.43)	1.6	0.69	6.8
<u>18c</u>	550	0.75 (0.98)	1.3	0.08	4.4

^a ± 5 nm. ^b $\pm 15\%$; the data in parentheses are in methanol.

^c $\pm 15\%$; the oxygen quenching rate constants were measured from triplet decay rates in air-saturated benzene (vs. those in degassed solutions).

homolytic cleavage of the C_2-O bond (Scheme III.5). Among these, the carbocation assignment seems very likely because of the phototropic photochemistry observed in the course of steady-state photolysis. Note that one would expect the photo-generated carbocations 2la,c to decay by mixed or second-order kinetics (i.e., by reaction with OR^- and/or reaction with hydroxylic solvent molecules). However, a close examination of the results reveals several facts that do not support the carbocation assignment. First, the observed difference spectrum due to the transient species in question in the region of ground-state absorption of 15a does not agree with that expected on the basis of the difference spectra of 15a and the carbocation 2la.³⁴ Specifically at 250-450 nm, the extinction coefficients of the carbocations are much higher than those of 15a and thus one would expect only positive absorbance change in this spectral region as a result of the carbocation formation from 15a (in disagreement with the bleaching observed at ~ 360 nm in methanol, Figure III.2, parts B and B'). Second, the extinction coefficient of the carbocation, as generated from 15a and 16a in strong sulphuric acid,³⁴ is not high enough at 600-800 nm to account for the laser-flash-photolytic absorbance changes in this region. A comparison of the end-of-pulse absorbance change at 720 nm for 15a in methanol with that due to benzophenone triplet at 520 nm in acetonitrile produced in optically matched solutions shows that the product of the extinction

Scheme III.5

coefficient and the photochemical yield of the carbocation would have to be $\geq 1200 \text{ M}^{-1} \text{ cm}^{-1}$ in order to be singly responsible for the absorbance changes at the long wavelengths. Since the photochemical yield is ≤ 1.0 , this means that the carbocation would have a band system at 600–800 nm with extinction coefficients $\geq 1200 \text{ M}^{-1} \text{ cm}^{-1}$. There is no way such a strong band system would remain undetected when 15a or 16a is dissolved in strong sulphuric acid (10 M). Third, the sensitivity of observed transients toward oxygen and HTEMPO is unusual for a carbocationic species in the ground state.

An assignment in terms of carbocation triplets would be interesting because there are precedents of photoadiabatic dehydroxylation in singlet excited state manifolds (e.g., 9-phenylxanthen-9-ol).²⁰ Note that such a process in the triplet manifold also would be spin allowed. From the onset of absorption of the carbocation from 15a (at $\sim 750 \text{ nm}$), the singlet energy (most probably S_1) is estimated at 38 kcal mol^{-1} . It is possible that the triplet energy (T_1) of the carbocation would be close to the excitation energy of singlet oxygen ($^1\text{O}_2^*$, $^1\Delta_g$), and hence the quenching of the carbocation triplets by $^3\text{O}_2$ may occur by an energy-transfer mechanism, albeit with a less than diffusion controlled rate constant (because of lack of exothermicity). Thus, the formation of singlet oxygen as a result of the oxygen quenching of the 750 nm transient in the case of 15a becomes explainable. The quenching by HTEMPO can also be explained by the spin-exchange mechanism.^{41–44} However,

on the following grounds, we are reluctant to accept the carbocation triplet assignment. First, since the carbocation triplets from 15a and 18a would be identical, their interaction with the base (OH^-) should occur in a similar manner. In practice, experiments with 18a in the presence of sodium hydroxide (0.4-0.8 M) in aqueous methanol do not show the decay/formation phenomena at 340-370 nm, as observed in the case of 15a. Second, an experiment was performed in which an attempt was made to sensitize the carbocation 21a to its triplet excited state. A methanolic solution of a mixture of 15a and erythrosin B (absorbances = 2.1 at 308 and 0.20 at 532 nm) was flash-photolyzed sequentially by two laser pulses at the two wavelengths, the second pulse (532 nm) being delayed by 14 μs relative to the first one (308 nm). At 308 nm, >95% of the laser photons was absorbed by 15a giving rise to the 750 nm species which decayed to the extent of $\sim 80\%$ during the interval (14 μs) before the arrival of the 532 nm laser pulse. The 532 nm laser pulse predominantly photolysed erythrosin B producing its triplet ($E_T = 44 \text{ kcal mol}^{-1}$)⁴⁵ which was monitored at 600 nm. Although the decay of the dye triplet was found to be enhanced when the first laser pulse (308 nm) was used to photolyse 15a (relative to the case in which 15a was not photolyzed), there was no indication for delayed formation of the 750 nm species as a result of possible energy transfer from the dye triplet to the photo-generated carbocation 21a.

For two reasons, we rule out the interpretation in terms of radicals derived from OR cleavage (path iii). First, one would not expect such radicals in the ground state to generate $^1\text{O}_2^*$ as a result of interaction with $^3\text{O}_2$. Second, for 15a in methanol, the $\cdot\text{OH}$ radical should react with the solvent, producing the reducing radical, $\cdot\text{CH}_2\text{OH}$; the formation of the latter should be detectable by its reaction with paraquat, PQ^{+2} (methyl viologen).⁴⁶ In laser flash experiments with 15a in the presence of 0.2-1.0 mM PQ^{+2} in methanol ($\lambda_{\text{ex}} = 337.1 \text{ nm}$), no growths of transient absorption due to the semi-reduced radical $\text{PQ}^{+\cdot}$ ($\lambda_{\text{max}} = 395 \text{ nm}$ and 615 nm) were observed at either absorption maximum.

Finally, we are left with the assignment in terms of the biradicals produced from $\text{C}_2\text{-O}$ bond cleavage (path iv). Such biradicals would represent the lowest triplet excited states of the corresponding enols (or enol-ethers) and may potentially interact with $^3\text{O}_2$ (by an energy transfer mechanism) and a nitroxy radical (by a spin exchange mechanism). Also, the differences in the acid-base behaviours of the transients from 15a and 18a become readily explainable in terms of the ketyl center at C_2 in the phototransients from 15a. The fact that we do not observe electron transfer from this transient (i.e., from the ketyl radical site) to PQ^{+2} is not disturbing, because the ketyl radicals from aromatic α -diketones (e.g., benzil and its 4,4'-dimethyl and 4,4'-dimethoxy analogues) have been shown to be unresponsive toward methyl viologen.⁴⁷

III.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or 580 infrared spectrometers. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. The ^1H NMR spectra were recorded on either Varian EM-390 or HA-100 NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a JEOL JMS-D 300 mass spectrometer at 70 eV. All steady-state irradiations were carried out either in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR 2537 or 3000 Å) or by using a Hanovia 450 W medium pressure mercury lamp in a quartz-jacketted immersion well.

III.4.1 Starting Materials. 2-Hydroxy -1-naphthaldehyde (12c),⁴⁸ mp 82-84 °C, dibenzoylacetylene (DBA, 13),^{49,50} mp 110-111 °C, 2,3-dibenzoyl-4H-1-benzopyran-4-ol (16a),³⁴ mp 137-138 °C, 2,3-dibenzoyl-4-methyl-4H-1-benzopyran-4-ol (16b),³⁴ mp 173-174 °C, 2,3-dibenzoyl-2H-1-benzopyran-2-ol (15a),³⁴ mp 170-171 °C, and 2,3-dibenzoyl-2-methoxy-2H-1-benzopyran (18a),³⁴ mp 110-111 °C were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

III.4.2 Preparation of 2,3-Dibenzoyl-1H-naphtho[2,1-b]pyran-1-ol (16c). A mixture of 12c (0.74 g, 4.3 mmol), 13 (1.0 g, 4.3 mmol) and anhydrous potassium carbonate (0.59 g, 4.3 mmol)

in acetone (10 mL) was stirred at 25 °C for 0.5 h and the inorganic material was removed by filtration. Removal of the solvent under vacuum gave a solid, which was recrystallized from a mixture (1:2) of benzene and petroleum ether to give 1.5 g (86%) of 16c, mp 165-166 °C.

IR spectrum ν_{\max} (KBr): 3510, 3440 (OH), 3050, 3020 (CH), 1665 and 1630 (C=O), 1610 and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (CH_3OH): 234 nm (ϵ , 40,800), 259 (25,500, sh), 271 (21,500, sh), 281 (16,600, sh), 311 (3,500, sh), and 325 (2,600, sh).

^1H NMR spectrum (CDCl_3): δ 3.37 (1 H, d, $J = 6$ Hz, D_2O -exchangeable, OH), 6.60 (1 H, d, $J = 6$ Hz, CH), and 6.78-8.03 (16 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 406 (M^+ , 2), 389 ($\text{M}^+ - \text{OH}$, 10), 388 ($\text{M}^+ - \text{H}_2\text{O}$, 10), 301 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 78), 300 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO} - \text{H}$, 65), 224 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO} - \text{C}_6\text{H}_5$, 47), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), and other peaks.

Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_4$: C, 79.80; H, 4.33. Found: C, 79.56; H, 4.68.

III.4.3 Preparation of 2,3-Dibenzoyl-4H-1-benzopyran-4-one (20a). A mixture of 16a (1.0 g, 2.8 mmol) and freshly prepared nickel peroxide^{51,52} (1.0 g) was stirred in benzene (20 mL) for 40 h at 25 °C. Removal of the inorganic material and the solvent gave a solid, which was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 0.95 g (96%) of 20a, mp 150-151 °C (lit.⁵³ mp 149-150 °C).

III.4.4 Irradiation of 2,3-Dibenzoyl-4H-1-benzopyran-4-ol (16a). A solution of 16a (500 mg, 1.4 mmol) in benzene (350 mL) was irradiated for 8 h (RPR, 3000 Å at 25 °C). The colour of the solution became blue initially, which turned dark yellow on prolonged irradiation. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and benzene gave 305 mg (61%) of 15a,³⁴ mp 171-172 °C (mixture mp), after recrystallization from a mixture (3:1) of benzene and petroleum ether.

In a blank run, a solution of 16a (100 mg, 0.28 mmol) in dry benzene (10 mL) was refluxed in the dark for 10 h. Removal of the solvent under vacuum, followed by recrystallization of the residual solid from a mixture (2:1) of benzene and petroleum ether gave 90 mg (90%) of the unchanged 16a, mp 137-138 °C (mixture mp).

In a repeat run, an acetone solution of 16a (500 mg, 1.4 mmol in 350 mL) was irradiated for 6 h and worked up as in the earlier case to give 370 mg (74%) of 15a, mp 171-172 °C (mixture mp).

In another run, a solution of 16a (500 mg, 1.4 mmol) in methanol (350 mL) was irradiated (RPR, 3000 Å) for 8 h. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 52 mg (10%) of 2,3-dibenzoyl-2-methoxy-2H-1-benzopyran (18a), mp 110-111 °C, after recrystallization from methanol.

IR spectrum ν_{\max} (KBr): 3050, 2970, 2825 (CH), 1700, 1650 (C=O), 1630, 1600 and 1570 (C=C) cm^{-1} .

UV spectrum λ_{\max} (CH_3OH): 245 nm (ϵ , 38,200), 295 (25,600), and 340 (11,400).

^1H NMR spectrum (CDCl_3): δ 3.54 (3 H, s, methoxy) and 7.15–8.20 (15 H, m, aromatic and vinylic).

Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_4$: C, 77.84; H, 4.86. Found: C, 77.61; H, 4.97.

Subsequent elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 260 mg (52%) of 15a, mp 171–172 °C (mixture mp).

Acid-Catalysed Conversion of 16a to 15a.³⁴ A solution of 16a (90 mg, 0.25 mmol) in methanol (10 mL), containing a small amount of hydrochloric acid (0.1 N, 1 mL) was refluxed for 10 min. Removal of the solvent under vacuum gave 70 mg (77%) of 15a, mp 170–171 °C (mixture mp), after recrystallization from a mixture (3:1) of benzene and petroleum ether.

Acid-Catalysed Conversion of 16a to 18a.³⁴ A solution of 16a (356 mg, 1 mmol) in dry methanol (10 mL) was refluxed with p-toluenesulphonic acid (0.1 N, 5 mL) for 1 h. The reaction mixture was cooled and then neutralized with pyridine. Removal of the solvent under vacuum gave a residual solid, which was extracted with ether. The ether-extract was washed with water, dried over anhydrous sodium sulphate and the solvent was removed

under vacuum to give 100 mg (28%) of 18a, mp 110-111 °C (mixture mp), after recrystallization from methanol.

III.4.5 Irradiation of 2,3-Dibenzoyl-4-methyl-4H-1-benzopyran-4-ol (16b). A solution of 16b (500 mg, 1.35 mmol) in benzene (350 mL) was irradiated (RPR, 2537 Å) for 3 h. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and ethyl acetate gave 300 mg (63%) of 19b, mp 220-221 °C, after recrystallization from a mixture (1:1) of acetone and petroleum ether.

IR spectrum ν_{\max} (KBr): 3045, 2940 (CH), 1670, 1635 (C=O), 1580 and 1570 (C=C) cm^{-1} .

UV spectrum λ_{\max} (THF): 257 nm (ϵ , 25,400) and 314 (3,600, sh).

^1H NMR spectrum (CDCl_3): δ 4.81 (1 H, s, methylene, 5.56 (1 H, s, methylene), and 7.15-8.21 (14 H, m, aromatic).

Mass spectrum, m/e (relative intensity): 352 (M^+ , 26), 323 (10), 298 (6), 247 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 5), 219 (10), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 62), and other peaks.

Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{O}_3$: C, 81.81; H, 4.54. Found: C, 81.57; H, 4.78.

In a repeat run, an acetone solution of 16b (500 mg, 1.35 mmol in 350 mL) was irradiated for 3 h and worked up as the earlier cases to give 275 mg (55%) of 19b, mp 220-221 °C (mixture mp).

In yet another run, irradiation of a solution of 16b (500 mg, 1.35 mmol) in methanol (350 mL) and workup as in the earlier cases, gave 310 mg (62%) of 19b, mp 220-221 °C (mixture mp).

Acid-Catalysed Conversion of 16b to 19b. A solution of 16b (200 mg, 0.54 mmol) in methanol (10 mL) containing hydrochloric acid (0.1 N, 5 mL) was refluxed for 5 min. The mixture, on cooling, was neutralised with pyridine. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and ethyl acetate gave 115 mg (60%) of 19b, mp 220-221 °C (mixture mp).

Conversion of 16b to 18b. To a solution of 16b (200 mg, 0.54 mmol) in methanol (10 mL), a solution of p-toluenesulphonic acid (0.1 N, 2 mL) was added at 10 °C and the mixture was stirred at 15-20 °C for 1 h. The solid that separated out, on cooling, was recrystallized from cold methanol to give 90 mg (44%) of 18b, mp 108-109 °C.

IR spectrum ν_{\max} (KBr): 3040, 3005, 2920, 2820 (CH), 1675 (C=O), 1590 and 1520 (C=C) cm^{-1} .

UV spectrum λ_{\max} (CH_3OH): 216 nm (ϵ , 35,000), 260 (15,000), 270 (14,000), and 302 (5,500).

^1H NMR spectrum (CDCl_3): δ 2.40 (3 H, s, CH_3), 3.49 (3 H, s, OCH_3), and 7.05-8.00 (14 H, m, aromatic).

Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_4$: C, 78.12; H, 5.20. Found: C, 77.85; H, 4.98.

III.4.6 Irradiation of 2,3-Dibenzoyl-1H-naphtho[2,1-b]-pyran-1-ol (16c). A solution of 16c (500 mg, 1.23 mmol) in benzene (350 mL) was irradiated (RPR, 2537 Å) for 8 h at 25 °C. Removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 100 mg (20%) of 22c, mp 209–210 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3040, 2980 (CH), 1700, 1650, 1640 (C=O), and 1590 (C=C) cm^{-1} .

UV spectrum λ_{\max} (CH_3OH): 226 nm (ϵ , 69,000, sh), 230 (69,000, sh), 256 (25,000), 328 (11,000), and 369 (17,000).

^1H NMR spectrum (CDCl_3): δ 7.17–8.38 (17 H, m, aromatic and vinylic) and 8.94 (1 H, s, aldehydic).

Mass spectrum, m/e (relative intensity): 406 (M^+ , 1), 301 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 3), 300 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, - H, 69), 299 (9), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100), 77 (C_6H_5^+ , 88), and other peaks.

Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_4$: C, 79.80; H, 4.43. Found: C, 79.62; H, 4.71.

Further elution of the column with benzene gave 220 mg (44%) of 15c, mp 195–196 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3360 (OH), 3060, 3045, 3020 (CH), 1683, 1660 (C=O), 1610 and 1590 (C=C) cm^{-1} .

UV spectrum λ_{max} (CH_3OH): 230 nm (ϵ , 46,200), 252 (25,100, sh), 322 (7,600, sh), 335 (8,800), and 384 (11,500).

^1H NMR spectrum (CDCl_3): δ 6.15 (1 H, s, D_2O -exchangeable, OH) and 7.05-8.25 (17 H, m, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 406 (M^+ , 2), 389 ($\text{M}^+ - \text{OH}$, 2), 388 ($\text{M}^+ - \text{H}_2\text{O}$, 2), 301 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 80), 224 ($\text{M}^+ - \text{C}_6\text{H}_5$, - $\text{C}_6\text{H}_5\text{CO}$, 62), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 66), 77 (C_6H_5^+ , 100), and other peaks.

Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{O}_4$: C, 79.80; H, 4.43. Found: C, 79.56; H, 4.59.

In a repeat run, irradiation of an acetone solution of 16c (500 mg, 1.23 mmol in 350 mL) for 4 h and workup as in the earlier cases gave 425 mg (85%) of 15c, mp 195-196 °C (mixture mp).

In another run, a solution of 16c (500 mg, 1.23 mmol) in methanol (350 mL) was irradiated (RPR, 2537 Å) for 6 h. Solvent was removed under vacuum and the residual solid was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 135 mg (26%) of 18c, mp 125-126 °C, after recrystallization from a mixture (1:2) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3045, 3020, 2945, 2915, 2840 (CH), 1700, 1630 ($\text{C}=\text{O}$), 1620, 1590, and 1570 ($\text{C}=\text{C}$) cm^{-1} .

UV spectrum λ_{max} (CH_3OH): 230 nm (ϵ , 48,300), 254 (28,000), 334 (9,300), and 381 (11,800).

^1H NMR spectrum (CDCl_3): δ 3.58 (3 H, s, methoxy) and 7.28-8.30 (17 H, m, aromatic and vinylic).

Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{O}_4$: C, 80.00; H, 4.76. Found: C, 79.74; H, 4.68.

Further elution of the column with benzene gave 200 mg (40%) of 15c, mp 195-196 °C (mixture mp), after recrystallization from a mixture (1:2) benzene and petroleum ether.

In a blank run, a solution of 16c (100 mg, 0.25 mmol) in methanol (15 mL) was refluxed in the dark for 8 h and worked up in the usual manner to give 90 mg (90%) of the unchanged 16c, mp 165-166 °C (mixture mp).

Acid-Catalysed Conversion of 16c to 15c. A solution of 16c (100 mg, 0.25 mmol) in methanol (10 mL), containing hydrochloric acid (0.1 N, 5 mL) was refluxed for 1 h. Removal of the solvent under vacuum gave a solid, which was extracted with ether and chromatographed over silica gel. Elution with benzene gave 52 mg (52%) of 15c, mp 195-196 °C (mixture mp).

Acid-Catalysed Conversion of 16c to 18c. To a solution of 16c (500 mg, 1.23 mmol) in dry methanol (20 mL), p-toluenesulfonic acid (0.1 N, 5 mL) was added and the mixture was refluxed for 4 h. The reaction mixture, on cooling, was neutralised with pyridine, poured into water and extracted with ether. Removal of ether under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 295 mg (57%) of 18c, mp 125-126 °C (mixture mp).

III.4.7 Irradiation of 2,3-Dibenzoyl-2H-1-benzopyran-2-ol (15a). A solution of 15a (500 mg, 1.4 mmol) in methanol (350 mL) was irradiated (RPR, 2537 Å) for 15 h. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 185 mg (36%) of 18a, mp 110-111 °C (mixture mp). Further elution with a mixture (9:1) of benzene and ethyl acetate gave 150 mg (30%) of the unchanged 15a, mp 171-172 °C (mixture mp).

In a blank run, a solution of 15a (100 mg, 0.28 mmol) in methanol (20 mL) was refluxed for 15 h and worked up in the usual manner to give 90 mg (90%) of the unchanged 15a, mp 171-172 °C (mixture mp).

Acid-Catalysed Conversion of 15a to 18a. A solution of 15a (356 mg, 1 mmol) in dry methanol (10 mL), containing a small amount of 98% sulphuric acid was refluxed for 20 h. The reaction mixture was cooled and neutralised with pyridine. Removal of the solvent under vacuum gave a product mixture, which was extracted with ether. The ether-extract was washed with water, dried over anhydrous sodium sulphate, and the solvent was removed under vacuum to give 150 mg (44%) of 18a, mp 110-111 °C (mixture mp), after recrystallization from methanol.

III.4.8 Attempted Photolysis of 2,3-Dibenzoyl-4-methylene 4H-1-benzopyran (19b). A solution of 19b (250 mg, 0.71 mmol) in benzene (300 mL) was irradiated (RPR, 2537 Å) for 25 h. Removal of the solvent under vacuum gave a residual solid,

which was chromatographed over silica gel. Elution with a mixture (9:1) of benzene and ethyl acetate gave 210 mg (84%) of the unchanged 19b, mp 220-221 °C (mixture mp).

In a repeat run, a solution of 19b (1.0 g, 2.84 mmol) in a mixture (9:1) of benzene and methanol (650 mL) was irradiated (Hanovia 450 W medium pressure mercury lamp in a quartz-jacketed immersion well) for 15 h. Workup of the photolysate as in the earlier case gave 650 mg (65%) of the unchanged 19b, mp 220-221 °C (mixture mp).

III.4.9 Attempted Photolysis of 2,3-Dibenzoyl-4H-1-benzopyran-4-one (20a). A solution of 20a (500 mg, 1.4 mmol) in benzene (500 mL) was irradiated (RPR, 2537 Å) for 26 h. Removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 300 mg (60%) of the unchanged 20a, mp 150-151 °C (mixture mp).

In a repeat run, a solution of 20a (500 mg, 1.4 mmol) in a mixture (2:1) of benzene and methanol (500 mL) was irradiated (RPR, 2537 Å) for 30 h. Workup as in the earlier case gave 325 mg (65%) of the unchanged 20a, mp 150-151 °C (mixture mp).

III.4.10 Laser Flash Photolysis.³⁹ The laser pulse excitation was usually carried out at 337.1 nm (2-3 mJ, ~8 ns), employing a UV 400 Molelectron nitrogen laser. For some experiments, use was also made of laser pulses at 355, 485, and 532 nm (Quanta-Ray DCR-1 Nd:YAG coupled with PDL-1 dye laser, 6 ns, <50 mJ) as well as at 308 nm (Lambda-Physik EMG MSC gas

excimer, 20 ns, ≤ 50 mJ). The transient phenomena were studied by using a kinetic spectrometer described elsewhere.⁵⁴⁻⁵⁶ The solvents used were benzene and methanol, and unless oxygen effects were meant to be studied, the solutions were deaerated by purging with argon. In experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solution for photolysis was allowed to flow from a reservoir through a 3 mm quartz cell.

III.5 REFERENCES AND NOTES

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